

MINERALOGICAL AND STRENGTH CHANGES DURING
SOIL - FLY ASH - LIME - GYPSUM STABILIZATION

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

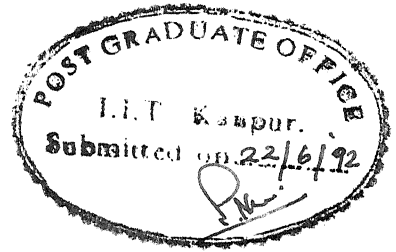
by
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to the
DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
JUNE, 1992

DEDICATED


TO

PARENTS



CERTIFICATE

It is certified that the work contained in the thesis entitled, "Mineralogical and Strength Changes during Soil - Fly Ash - Lime - Gypsum Stabilization", by Sanjay Kumar Shukla has been carried under my supervision and that this work has not been submitted elsewhere for a degree.


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LEGEND FOR FIGURES 4.1. TO 4.6

L	-	Calcium hydroxide [$\text{Ca}(\text{OH})_2$]
T	-	Tobermorite [$\text{Ca}_5 (\text{Si}_6\text{O}_{18}\text{H}_2) \cdot 4\text{H}_2\text{O}$]
C_1^*	-	Calcium silicate hydrate [$0.8 - 1.5 \text{ CaO} \cdot \text{SiO}_2 \cdot 0.5 - 2.5 \text{ H}_2\text{O}$]
C_2^*	-	Calcium silicate hydrate ($1.5 - 2.0 \text{ CaO} \cdot \text{SiO}_2 \cdot 1 - 4 \text{ H}_2\text{O}$)
C_3	-	Dicalcium aluminate silicate 8-hydrate [Strätling's compound, C_2ASH_8 perhaps $\text{Ca}_2\text{Al}_2(\text{OH})_6(\text{SiO}_4) \cdot 5\text{H}_2\text{O}$]
E	-	Ettringite [$\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$]
T_4	-	Tetracalcium aluminate 13 - hydrate ($\text{C}_4 \text{AH}_{13}$)
H	-	Hydrogarnet

* C_1 and C_2 are respectively denoted by CSHI and CHSII.
 In cement chemistry different abbreviations are used for
 different oxides, such as C = CaO, A = Al_2O_3 , S = SiO_2 and
 H = H_2O .

ABSTRACT

Mineralogical changes and strength development in a red soil stabilized with fly ash - lime - gypsum (FLG cement) on ageing were investigated. The soil chosen was from Daltonganj (Bihar) and is composed of quartz, iron and aluminium oxides, muscovite and kaolinite. Fly ash from the thermal power plant at Panki (Kanpur) has in its composition high quartz, mullite, alumina as well as calcium oxide.

X-ray diffractograms obtained at different stages of ageing upto 28 days revealed that in case of hydrated cement, ettringite ($C_3A.3CaSO_4.32H_2O$) was the only product present in the very initial period of ageing, while during the latter part of the ageing period tetracalcium aluminate 13-hydrate (C_4AH_{13}), calcium silicate hydrate (CSH I) and 11Å tobermorite [$Ca_5(Si_6O_{18}H_2).4H_2O$] were the products. On the other hand, in case of soil stabilized with the same cement gehlenite hydrate (Strätling's compound, C_2ASH_8) and hydrogarnet formed in addition to those mentioned above. Further, CSH II was the species for the calcium silicate hydrate in the case of stabilized soils. Gehlenite hydrate is metastable and with lime and gypsum, it converts gradually either into hydrogarnet or ettringite depending on whether the cement used for stabilization is less (4 to 8 %) or more (12 to 20 %). The reactions in the soil-cement systems are chemically controlled. The high pH facilitates easy dissolution of silica and alumina which contribute to the formation of the reaction

and alumina which contribute to the formation of the reaction products. With time as the products grow, the pH gradually, reduces in the system.

All the cementitious products formed were also identified in the scanning electron micrographs and their morphological characteristics described. The reaction appeared to have been initiated around the grain boundaries which progressed with time towards the grain interior.

Unconfined compressive strength data revealed that in the case of soil stabilized with 12 %, 16 % and 20 % cement, strength improvements are substantial (about 15 to 20 times the original strength). The initial strength was caused mainly by ettringite while calcium aluminate hydrate and silicate hydrate species were responsible for latter strengths.

CHAPTER 1

INTRODUCTION AND SCOPE OF STUDY

Red soils cover a substantial area in the world particularly in semi-arid and humid tropical regions. In India, they are distributed at several places and in general, occur surrounding the black soils and also along the slopes and higher reaches of the hilly terrain such as in the Rajmahal hills. These soils cause serious problems in terms of pavement failures both on highways and air fields and also the slope failures. The soils are highly susceptible to erosion. The cohesion in the soil is very low and the shear strength is attributed substantially (of about 80 %) to the internal friction (Uehara and Gillman, 1980).

Stabilization of red soils can be carried out using chemical additives. Besides lime, fly ash offers an immense potentiality for its use in the same. Fly ash is a by-product available as a waste material at any thermal power plant site in India. It may be noted here that the power generation through thermal power plants in India has been raised to 21,500 mW in 1990 from around 3,500 mW in 1960, resulting in the increase in fly ash generation from 6 to 30 million tons per year. Fly ash has been used by earliest workers in the manufacture of Portland cement, pozzolana cement, brick manufacture, light-weight sintered aggregates besides its being used as a filler material. Red soils can be

satisfactorily stabilized both with fly ash alone as well as with lime-fly ash (Ghosh et al., 1979). Remarkable improvement has been reported in CBR-values when stabilized with lime and fly ash. Few examples of utilization of fly ash in India in pavement construction are indicated in Table 1.1.

Although extensive work has been carried out for the last 2 to 3 decades on utilization of fly ash in conjunction with lime (as detailed in Chapter 2), not enough work is available dealing with the mineralogical changes in the system as related to strength behaviour. In this regard, techniques like x-ray diffraction and electron microscopy play a vital role in enabling a greater understanding of the changes occurring within a soil-fly ash-lime system. Once the cementitious products are identified at different stages of ageing, efforts can be directed to create favourable chemical conditions in a system that can result in strength-imparting products of a desired type. With this objective in view, gypsum has been used in conjunction with lime and fly ash for the stabilization of red soils.

The present study has been conducted to arrive at an understanding on the following aspects :

1. Mineralogical changes that take place in soil-fly ash-lime-gypsum system.
2. Role of gypsum in the nature of compounds produced.

Table 1.1

Use of Fly Ash in Pavements*

Sl. No.	Specification of work	Location and adoption as reported by C.R.R.I.	Year Of Use	Performance
1.	Lime-Fly ash stabilized soil as sub-base in pavement sub-base construction	(a) Sector 16A of Faridabad township, Haryana (Used as course)	1972	Satisfactor
		(b) NH 2 near Ballabgarh, Haryana. (Used as sub-base course)	1974	Satisfactor
		(c) Talchar-Gopalprasad Kaniha road, Orissa	1976	Satisfactor
		(d) Ghaziabad bypass on NH 24. (Used as sub-base course)	1981-82	Very Satisfactor
2.	Cement-fly ash concrete	(a) Taxi track Palam airport, Delhi. (Used as wearing course)	1970-71	Satisfactor
		(b) Transport vehicle workshop, Rewari (Used as wearing course)	1972	Very Satisfactor
		(c) Taxi-track at Pune air field, Maharashtra (Used as wearing courses)	1976-77	Satisfactor
3.	Lean cement-fly ash concrete	(a) Ghaziabad bypass on NH 24, (Used as sub-base course)	1980-81	Satisfactor
		(b) Flood prone Khadar area of Panipat, Haryana (Used as sub-base course)	1981-82	Very Satisfactor

* after Sheera and Arora, 1988.

3. Strength variations in the soil-additive system during ageing as related to the growth of compounds with time.
4. Based on the investigations, the feasibility of utilization of fly ash in the form of fly ash-lime-gypsum (FLG) cement for soil stabilization.

The material presented in this thesis is organized into seven chapters. While the topic is introduced and the scope of the work defined in this (Chapter 1), the existing literature is reviewed in Chapter 2. In Chapter 3, the material chosen and the methods adopted pertaining to the investigations are detailed. The characterization of the reaction products, their growth patterns with ageing of the systems as well as the morphological characteristics are detailed in Chapters 4 and 5 respectively. Development of strength in the hydrated FLG cement and soil stabilized with FLG cement is discussed in Chapter 6. An integrated picture is briefly projected in Chapter 7.

CHAPTER 2

EXISTING LITERATURE

2.1 General

Soil stabilization in its broadest sense is the alteration of any property of a soil to improve its engineering performance. Examples of soil improvement are increased strength (as for a pavement subgrade), reduced compressibility (as for the foundation of a structure), and reduced permeability (as for the foundation of a dam) (Lambe and Whitman, 1979). Soil stabilization techniques can be grouped under two main types : (a) improvement of a soil property of the existing soil without any admixture, and (b) improvement of the properties with the help of admixtures. In literature there are many types of admixtures such as ordinary Portland cement, lime, fly ash, bitumen, calcium chloride, sodium chloride, sodium carbonate, sodium sulphate, sodium silicate, rice husk ash, and gypsum. In the present work fly ash, lime and gypsum were used as admixtures and so the literature review is mainly restricted to the work done with these materials.

Role of various chemicals (some discussed above) in strength development and procedure for the effective way of mixing and compacting of soil-cement mixtures during construction at sites have also been investigated during the past three decades.

Attempts have also been made by earlier workers to use industrial wastes like fly ash and rice husk ash either directly or with cement or lime (Davidson et al., 1958 ; Vincent et al., 1961; Gokhale and Swaminathan, 1973; Gokhale and Guru Prasad, 1975; Funston et al., 1984; Krell, 1989; Osula, 1991).

2.2 Role of Fly Ash as an Admixture

Fly ash is formed during the burning of coal for power generation in a thermal power plant. This material is collected by any suitable device such as cyclone separator or electro-precipitator. The primary constituents of fly ash are microscopic in size and generally composed of spherical granules chiefly of silica, alumina, iron and calcium oxides. These granules are formed when small silicate and aluminosilicate particles within the coal are exposed to temperatures around 1200°C to 1400°C in the combustion chamber. The fly ash is then, for the most part, a heterogeneous mixture of highly vitreous spherical particles, crystalline matter and unburnt coal. The nature and quantity of fly ash generated depends upon a number of factors like

- (1) coal source,
- (2) degree of coal pulverization,
- (3) boiler unit design,
- (4) loading and firing conditions,
- (5) ash collection and processing methods,
- (6) fly ash storage methods, and
- (7) air - fuel ratio.

Fly ash is classified as a pozzolanic material. A pozzolana is defined as siliceous and aluminous material which, in finely divided form and in the presence of moisture, will react with calcium hydroxide (or slaked lime) to form compounds possessing cementitious properties. The pozzolanic reaction takes place when the silica and alumina chemically react with any slaked lime present in the system. Some fly ashes possess the capability to exhibit a cementitious reaction in the presence of moisture. This capability comes from sufficient levels of calcium silicates and is much faster than pozzolanic reaction. This reaction is similar to that which occurs in the hydration of ordinary Portland cement. Several features of fly ash are detailed in the Code IS : 3812 - 1981.

2.2.1 In cement production

Fly ash has potential application in cement production both as a raw material for ordinary Portland cement (OPC) and as an admixture to OPC in the production of Portland pozzolana cement (PPC). Use of fly ash as a part replacement of cement and as an admixture is outlined in Code IS : 456 - 1978. The requirements of lime pozzolana mixture produced by the intergrinding or blending of lime and fly ash are presented in Code IS : 4098- 1967, while the requirements of PPC manufactured either by intergrinding OPC clinker and fly ash with addition of gypsum, or by blending OPC and fly ash are covered in IS : 1489 - 1976. Though there are special cases wherein clinkers accept up to 50 % of fly ash, in general the quantity

of fly ash is in the range of 15 - 30 % as per the cement standards of the world.

Fly ash is the main constituent of Fly ash - Lime - Gypsum (FLG) cement that has emerged as the formidable cementitious product in the International construction scenario, and has opened up a new avenue of its utilization. FLG cement is a ground blend of fly ash, lime and calcined gypsum, in suitable proportions which on hydration yields strengths rendering a totally water - impervious hard matrix. This makes obvious the formation of mineralogical phases during hydration similar to those in ordinary Portland cement. Hence FLG cement can be used as a substitute to OPC in various applications such as soil stabilization and to develop FLG concrete and mortar. The production of OPC involves burning of raw materials at a temperature range of 1300 - 1400°C that consumes a thermal energy of about 900 K Cal per kg, making it an energy intensive product. FLG cement technology involves low energy consumption (100 to 200 KCal/kg of the cement produced, roughly about 1/9 of the energy involved in OPC). In addition, the cement plant size can vary depending on its location, thus making it convenient for a rural scene.

2.2.2 In cement concrete

Fly ash can be used as a part replacement of fine aggregate (IS : 3812, part III - 1966) and also as an admixture for concrete (IS : 3812, part II - 1966). Reshi and Garg (1988) working on the use of different types of fly ash as Pozzolana,

admixture or as fine aggregate in mortar and concrete reported that all the types are found suitable for use as pozzolana replacing 20 to 25 per cent of cement. They also reported that it can be advantageously used to replace sand in mortar and concrete. Lal (1988) reported that replacement of cement by fly ash upto 20 per cent by weight in concrete and mortar does not adversely affect the strength of the resultant mix. Projects, on experimental basis, for the use of fly ash as partial replacement of cement were undertaken in India by the National Building Organisation. Some are :

- (1) Building construction in R.K. Puram, New Delhi : cement was replaced by fly ash upto 20 % and was tried in concrete as well as mortars
- (2) Building construction in Dhaulakuan, New Delhi : replacement of 20 % cement by fly ash was tried in the project for constructing four - storeyed blocks of 16 type III quarters.
- (3) Building construction in Basant Nagar, Madras : cement was partially replaced by fly ash in the project for constructing 144 middle income group flats.
- (4) Construction of precast R.C.C. components with fly ash replacing cement upto 15 % by Hindustan Prefab. Ltd., New Delhi.

For most of the mass concrete applications for marine and aggressive water zones, use of fly ash as a part replacement to OPC has been established without sacrificing the ultimate concrete qualities, owing to certain advantages as given below :

- (1) Equal consistency and workability level with OPC concrete at low water requirement because of the existence of spherical particles in fly ash.
- (2) Low heat of hydration contributing for less thermal cracks of concrete.
- (3) High impermeability levels because of denseness of concrete resulted out of fines of fly ash which contribute to filling of pores of concrete.
- (4) High resistance to sulphate - bearing water.

Funston et al. (1984) reported that fly ash with 4 to 5 % of cement and appropriate amount of water can be used as a new backfill material, which will flow into place without sophisticated construction techniques. This backfill material also was proved to be of good quality and economical over the conventional backfill materials. Krell (1989) showed experimentally that flowable fly ash has better physical properties than conventional structural backfill and is economically competitive with the same. Brook et al. (1990)

reported that fly ash improves the properties of both fresh and hardened concrete. In fresh concrete it reduces water demand, improves workability and reduces bleeding and segregation whereas in hardened concrete, it increases subsequent compressive and tensile strengths and reduces permeability.

2.3 Stabilization

2.3.1 Soil - fly ash system

Studies on soil stabilization with fly ash alone have been reported by Mateos and Davidson (1962), Sharma (1965), Singh (1967), Uppal and Dhawan (1968) as well as Gokhale and Guru Prasad (1975). These studies established that with the increase of the percentage of the fly ash, there is an increase of the optimum moisture content as well as a decrease of the maximum dry density. The entire strength development was reported to have taken place in the initial period of ageing itself. The x-ray diffraction data revealed that no new compounds were formed and thus fly ash acts as a physical bonding material. Addition of fly ash beyond the required amount to a soil results in the decrease of strength.

2.3.2 Soil-lime system

The response of a cohesive soil to treatment with lime is complex and often dramatic. Improvements in engineering properties for the soil on stabilization were attributed to four basic reactions by earlier workers :

- (1) Cation exchange i.e. replacement of exchangeable sodium, magnesium or other cations previously held by the soil - clay by calcium cations derived from the lime.
- (2) Flocculation of the clay and the consequent increase in effective grain size.
- (3) Carbonation i.e. reaction of lime with carbon dioxide from the atmosphere to form calcium carbonate which was considered to be responsible for the cementing action.
- (4) Pozzolanic reactions with soil constituents to generate new minerals of a cementitious nature.

Cation exchange plays an active role in the initial stages of lime treatment with fixation of calcium ions in the clay. However, cation exchange alone as a possible mechanism for soil - lime reactions has been discounted from different considerations. Although, flocculation modifies the soil fabric thus contributing to a change in the engineering behaviour, it is only one of the factor and not the sole controlling parameter in the process of lime stabilization. Eades, Nichols and Grim (1962) have established that carbonation of lime in the soil - lime specimens takes place if exposed to the atmosphere. However, carbonation does not contribute to the stabilization process to the extent postulated by several workers. Carbonation, in fact, is an undesirable factor for stabilization because it reduces the effectivity of the lime otherwise available for the reaction.

Since all these factors are inadequate in explaining the process of stabilization, Diamond and Kinter (1965) have proposed two distinct stages of reactions.

1. Short term changes :

- (a) A large increase in the plastic limit generally followed by a reduction in the plasticity index.
- (b) A sharp reduction in the apparent content of clay - size particles as they are bound into flocs.
- (c) Increase in the moisture and compactive effort required to achieve a given density.
- (d) Reduction in swell pressure, volume change on drying and permeability.

With the addition of lime, these changes occur in periods ranging from minutes to a few hours.

In general, there is an universal agreement on the observation that the addition of lime results in the decrease of plasticity index with increasing plastic limit (Hilt and Davidson, 1960; Osulo, 1991). However, conflicting reports exist on the effect of lime on the liquid limit. Wang et al.(1963), Jan and Walker (1963) as well as Osulo (1991) reported a decrease in the liquid limit while a substantial increase in the liquid limit has been reported by Clare and Cruchley (1957) and Zolkov (1962).

Apparently this variation has been due to the sensitive nature of the clay to the cation present (Grim, 1968). Drastic volume changes involved in the clay - lime stabilization have been discussed by Lund and Ramsey (1959), Croft (1964) and Katti et al. (1966). Formation of reaction products has also been reported even in the first few days of lime treatment of soils. Diamond (1964) has reported the slow and restricted formation of the well - crystallized tetracalcium aluminate hydrate $(C_4AH_{13})^*$. Subsequently Diamond and Kinter (1965) have observed the formation of calcium silicate hydrate (tobermorite gel) in extremely limited quantity in addition to the tetracalcium aluminate hydrate. But the presence of the compounds, according to these authors could not be demonstrated due to their limited amounts and poor crystallization. The strength developed depends to some extent on the kind of the cementing agent formed and also to a greater extent on the proportion of void space occupied by the cementing agent - the "gel - space ratio", similar in cement technology (Jambor, 1963).

2. Long term changes :

The reactions occurring over a long period of time contribute significantly to strength gain. The cementitious

* C,A,S and H stand for CaO , Al_2O_3 , SiO_2 and H_2O respectively (as in cement terminology).

products formed by reactions between common clay minerals and lime have been studied by workers including Eades and Grim (1960), Slone (1964), Croft (1964), Diamond and Kinter (1965), Davidson et al. (1966), Gokhale and Guru Prasad (1975). Distinction can be made between the products formed by rapid reactions after short curing and those crystallizing after longer periods. Short - term strengths, with all clay minerals, are attributed to formation of mixed gelatinous and "structurally ordered" phases. Polymorphic varieties of C_4AH_{13} in the initial stages and CSHI during the final stages were identified in the clay - lime reactions. Enhanced strengths on long term ageing are attributed to the formation of tobermorite group of minerals consisting of calcium silicate hydrates of a variable composition. The individual species in this group are identified on the basis of their basal spacings in the x - ray diffraction patterns (Taylor, 1965). In cement research, several species of the hydrated products have been identified. However, in soil - lime stabilization, formation of compounds like CSHI, CSHII and tobermorite either in gel form or as a well crystallized product has been reported. CSHII is a high calcium phase as compared to CSHI. Very little information regarding the mechanism of soil - lime stabilization exists in the literature. The earliest was by Eades and Grim (1960) who reported the eating up of edges of kaolinite by lime during reaction. This was later confirmed by Diamond, White and Dolch (1963). Several workers like Sloane (1964 and 1965), Wolfe and Allen (1964) have proposed the mechanism of product formation.

2.3.3 Soil - fly ash - lime system

Studies of soil-fly ash-lime have been reported by several workers such as Mateos and Davidson (1962), Ghosh et al. (1973), Singh (1967), Gokhale and Guru Prasad (1975), Ghosh et al. (1979). According to Croft (1963) fly ash is less responsive to lime compared to the common clay minerals. The short - term strengths developed in compacted mixtures due to lime - clay reactions were lower than those usually attained with lime, and hence the differences were attributed to the influence of fly ash. Reactions between lime and fly ash proceeded slowly and contributed to strength after longer curing periods than with clay minerals. New minerals formed in lime-fly ash reaction products included varieties of C_4AH_{13} and CSHI. Reductions in compacted densities may result from the addition of "silt - size" fly ash to clay - soils. Materials deficient in particles of this size are most suitable for lime-fly ash treatment and include certain sandy - clays, natural and artificial gravels, and crushed stone. Lime is more suitable for stabilizing clay - soils than lime - fly ash mixtures. Addition of lime to a remoulded soil improves the "tilth" and "workability" and promotes an even dissemination of the fly ash particles throughout. Spherical flocculated aggregates of soil, lime and fly ash are produced during mixing and retain their shape during compaction. Early lime - clay reactions are responsible for intra - aggregate cementation; but fly ash particles tend to be inert and weaken the material by interrupting the continuity of the cementitious bonds. Inter-

aggregate linkages form, but more slowly than lime - clay mineral mixtures. Fly ash contributes to improved compacted densities, and frictional forces between particles are regarded as responsible for supporting early - applied loads. If small amounts of clay are present, lime - clay reactions are responsible for early strengths. The development of long - term strength is attributed to intergrowths of crystalline minerals, and hardening of gelatinous phases; bond formed between lime, clay and fly ash particles, and flocculated aggregates. Deformation in stabilized specimens proved to be greater for materials with higher clay contents.

2.3.4 Soil - fly ash - lime - gypsum system

Information available on this system is rather scanty. Ghosh et al. (1979) reported that the compressive strength and CBR^{*} - value of lime - fly ash stabilized alluvial soil could be further improved by incorporation of one per cent gypsum (by weight of lime, fly ash and soil) as an additive. Some improvements were also observed with other additives such as sodium carbonate and calcium chloride. Addition of one per cent gypsum was found to be the most suitable from the point of improvement in CBR - value, economy and engineering requirements. According to some workers, the alumina of fly ash has a negligible role to play, if it is purely in the presence of lime, by forming into gehlenite hydrate (C_2ASH_8) which is

* CBR stands for California Bearing Ratio.

hydraulically an inert material. This is attributed as the reason for weak strength of fly ash in spite of its lime reactivity. In order to get the benefit of alumina, normally gypsum is added to improve the amount of ettringite ($C_3A \cdot 3 CaSO_4 \cdot 31 - 32 H_2O$), a relatively strong and water impermeable constituent. This ettringite, which is formed within a regulated pace and quantum, accelerates the setting rate and increases the early strength.

CHAPTER 3

MATERIALS AND METHODS

3.1 General

The materials involved in the study are red soil, fly ash, lime and calcined gypsum. This chapter deals with the physical and mineralogical characterization of these materials. Different techniques used in the present study are detailed.

3.2 Materials Used

3.2.1 Soil

The soil chosen for the study was collected at Daltonganj in Palamau district (Bihar). Pavement failure is a common feature in this region. The soil is red in colour, moderately plastic and has 44 % clay fraction. The grain size distribution curve is indicated in Fig. 3.1. Physical and index properties of this soil are presented in Table 3.1. The x-ray diffractogram of soil (Fig. 3.2) reveals that this soil is rich in quartz with subordinate amounts of kaolinite, muscovite and also the secondary oxides of iron and aluminium. The characteristic reflections for these mineral constituents are indicated in Table 3.2.

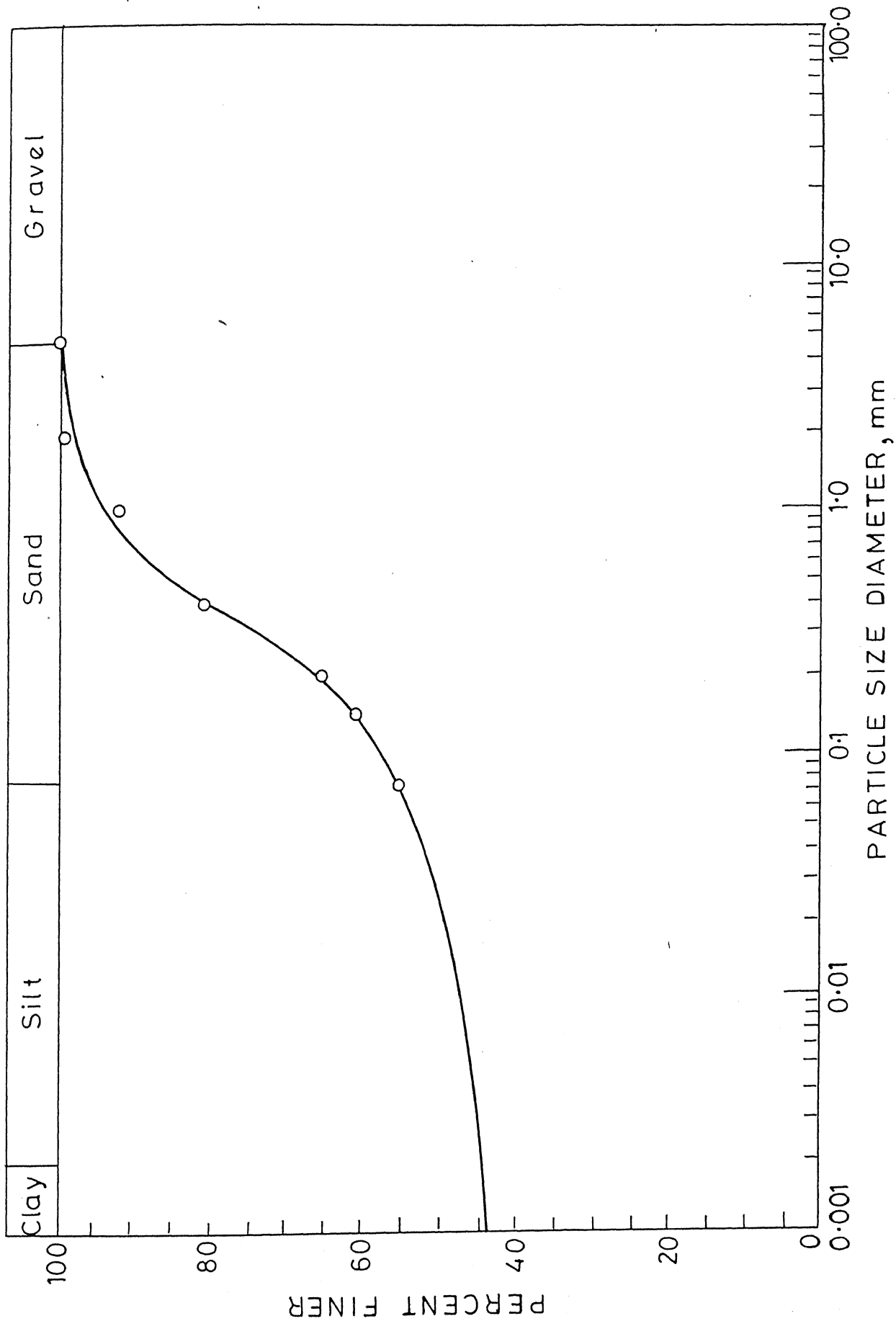


Fig. 3.1 Grain size distribution curve of the soil

Table 3.1
Physical and Index Properties of Soil

Clay (<0.002 mm) (%)	44
Silt (0.06 - 0.002 mm) (%)	12
Sand (2 - 0.06 mm) (%)	44
Specific gravity (G)	2.59
Liquid limit (W_L) (%)	32.0
Plastic limit (W_p) (%)	16.3
Shrinkage limit (W_s) (%)	13.2
Plasticity index (I_p) (%)	15.7
Flow index (I_f) (%)	13.8
Toughness index (I_t)	1.14
Shrinkage ratio (SR)	1.9
Optimum moisture content (%)	11.0
Maximum dry density at OMC (gm/cc)	2.03
Unconfined compressive strength (MPa)	0.038
pH*	9.14
Soil classification	CL**

* pH was measured in accordance with procedure indicated in section 3.3.5.

** CL stands for inorganic clays of low to medium plasticity in Unified Soil Classification.

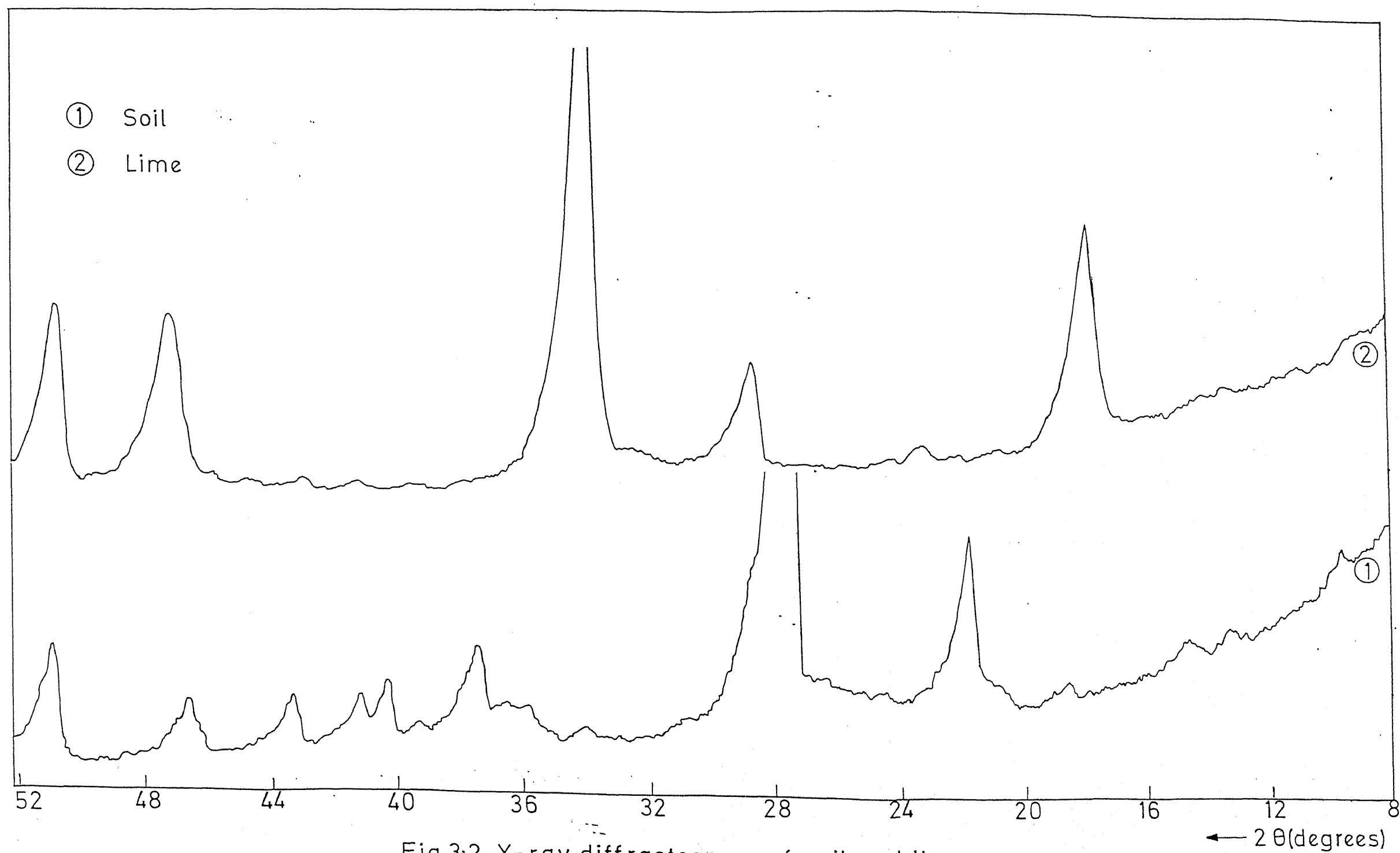


Fig.3.2 X-ray diffractograms of soil and lime
(Radiation used: $\text{CuK}\alpha$)

Table 3.2

X-ray Diffraction Data of the Soil

2θ (degrees)	d (\AA°)	Constituents
9.85	9.99	Muscovite
12.38	7.15	Kaolinite
14.13	6.27	Lepidocrocite
14.54	6.09	Boehmite
18.29	4.85	Gibbsite
19.87	4.47	Muscovite
20.32	4.37	Gibbsite
20.85	4.26	Quartz
22.35	3.98	Diaspore
23.70	3.754	Plagioclase
		Feldspar
24.25	3.67	Hematite
24.92	3.573	Kaolinite
25.50	3.49	α - Alumina
26.62	3.349	Quartz
27.90	3.20	Plagioclase
		Feldspar

Table 3.2. (continued)

2θ (degrees)	d (\AA°)	Constituents
28.30	3.15	Boehmite
33.30	2.69	Hematite
35.05	2.56	Muscovite
35.71	2.514	Hematite
36.25	2.478	Lepidocrocite
36.50	2.46	Quartz
37.80	2.38	Gibbsite
38.40	2.34	Kaolinite
39.35	2.29	Quartz
40.23	2.242	Quartz
40.95	2.204	Hematite
42.42	2.13	Quartz
45.59	1.99	Muscovite
45.80	1.98	Quartz
46.90	1.94	Lepidocrocite
49.60	1.838	Hematite
50.10	1.821	Quartz

3.2.2. Fly ash

In the present work, fly ash from the Thermal Power Plant at Panki (Kanpur) was used. It is grey in colour and has about 76 % silt - size and 24 % sand-size particles. The chemical composition and physical properties of this fly ash are given in Table 3.3. The x-ray diffractogram of fly ash is indicated in Fig. 3.3. and its characteristic reflections are listed in Table 3.4. Presence of CaO as a minor constituent can be identified from low intensity peaks at 1.701 \AA and $2.778^{\circ} 2\theta$.

3.2.3. Lime

Calcium hydroxide (hydrated lime) was prepared in the laboratory by slaking of commercial quick lime (CaO) in powder form. The x-ray diffractogram of this material (Fig. 3.2) revealed its high purity as evidenced from the presence of all its peaks. Absence of peaks of any impurity item confirms that the impurities, if any, are below 2 % which is the detectable limit in the x-ray diffractogram.

3.2.4 Calcined gypsum

Gypsum used in this study was obtained from the ACC cement plant at Sindri (Bihar). Calcination of this material was carried out in the laboratory at about 160°C for 6 hours. The dehydration involved in the conversion of gypsum to the calcined product is as follows :

Table 3.3

Chemical Composition^{*} and Physical Properties of Panki Fly Ash

Chemical composition (per cent)

SiO_2	57.01
Al_2O_3	22.83
Fe_2O_3	6.66
CaO	3.34
MgO	1.77
SO_3	0.56
Specific gravity	2.14
Optimum moisture content (%)	33.6
Maximum dry density at OMC (gm/cc)	1.15

(* after Ghosh et al., 1973).

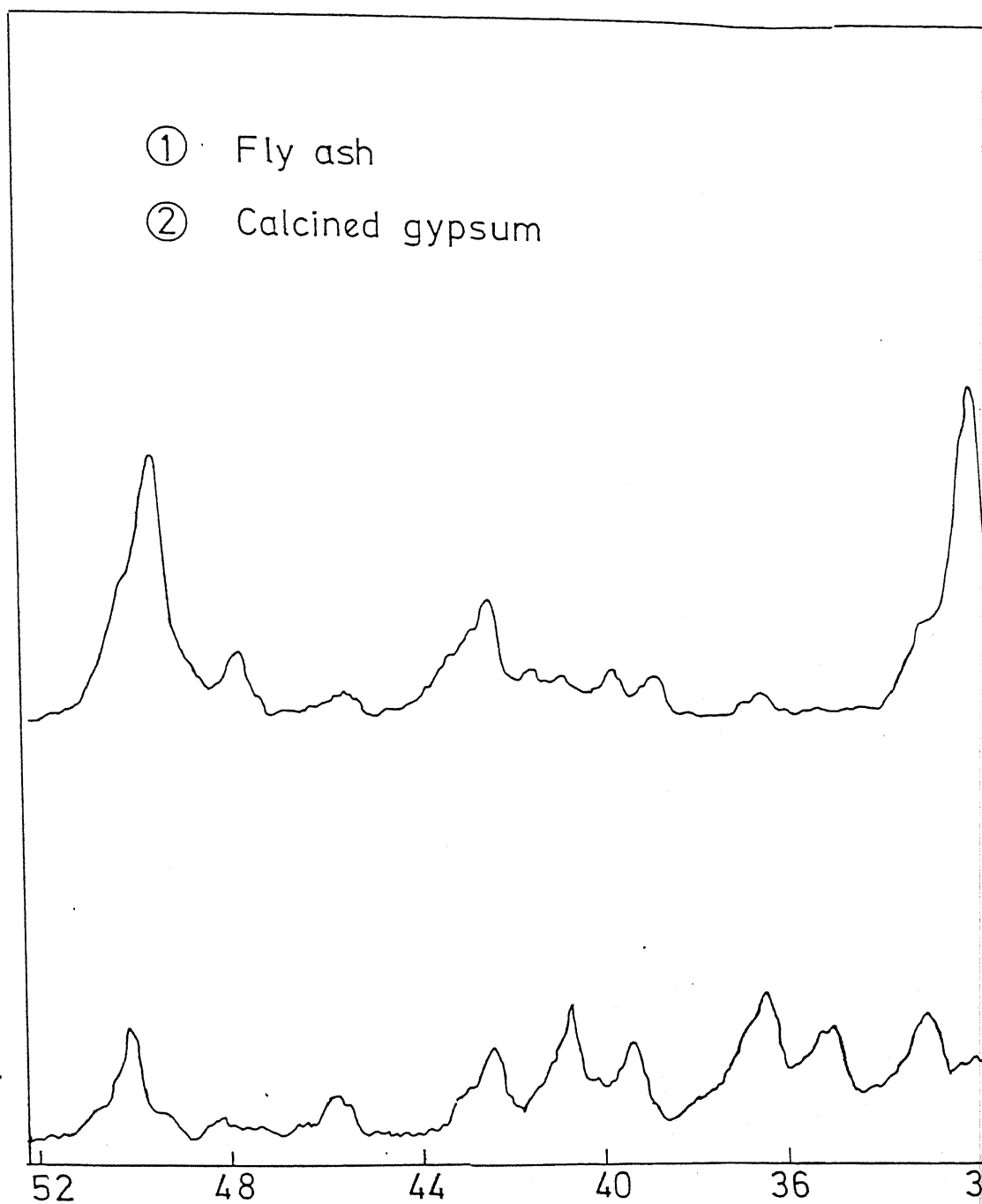
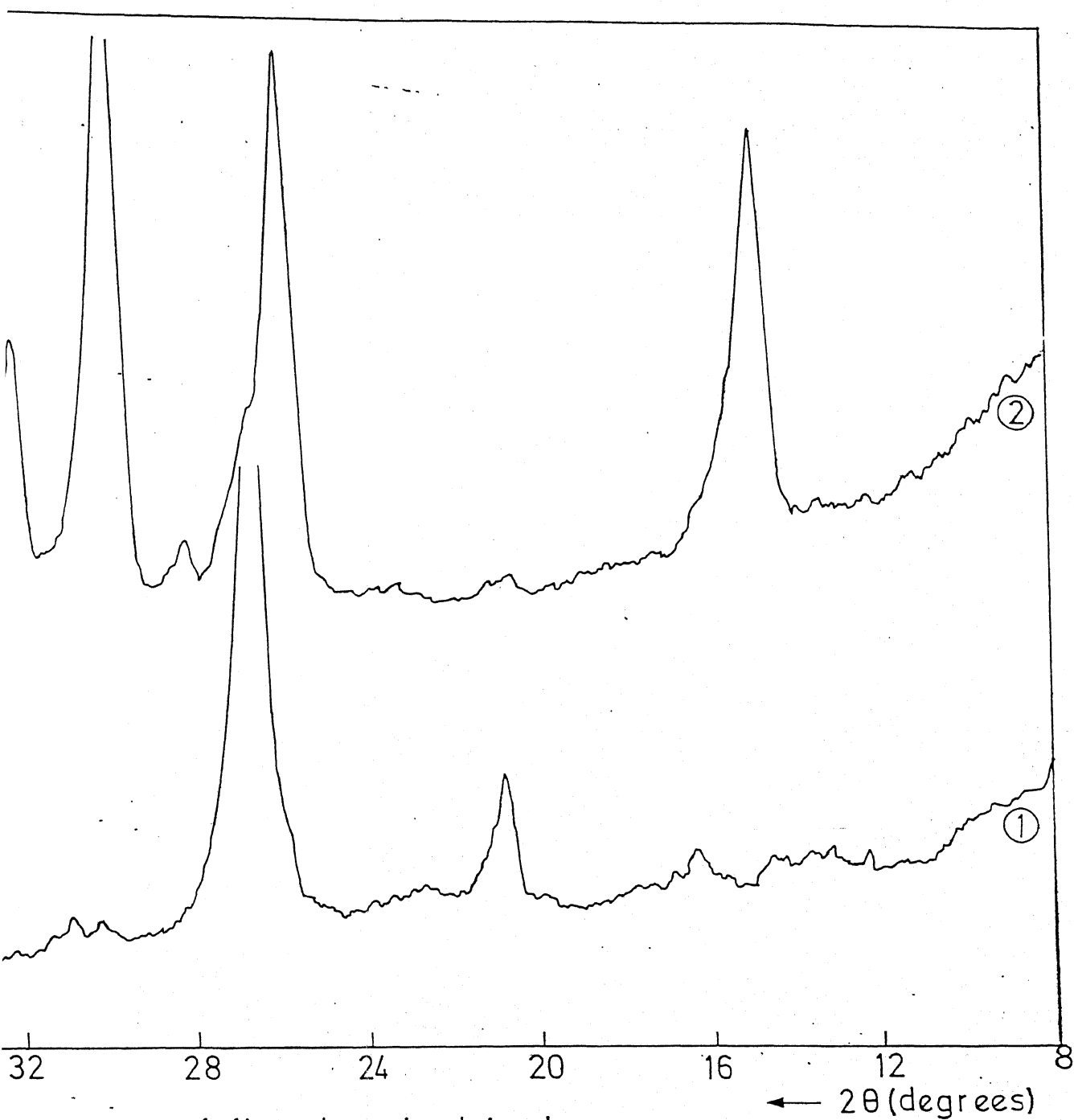


Fig.3-3 X-ray diffraction patterns
(Radiation: $\text{CuK}\alpha$)



actograms of fly ash and calcined gypsum
ation used: $\text{CuK}\alpha$)

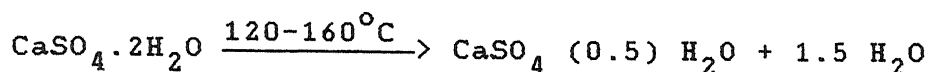
Table 3.4

X-ray Diffraction Data of Panki Fly Ash

2 θ (degrees)	d(\AA)	Constituents
16.40	5.40	Mullite
20.65	4.30	Tridymite
20.85	4.26	Quartz
21.78	4.08	Tridymite
26.07	3.418	Mullite
26.67	3.343	Quartz
31.40	2.85	θ -Alumina
32.22	2.778	Calcium oxide
32.93	2.72	θ -Alumina
33.20	2.699	Iron oxide
33.35	2.686	Mullite
35.11	2.556	Iron oxide
35.36	2.538	Mullite
35.71	2.514	Iron oxide
36.45	2.47	Quartz

Table 3.4 (continued)

2θ (degrees)	d (Å)	Constituents
36.85	2.439	θ -Alumina
39.40	2.29	Quartz
40.72	2.22	Iron oxide
42.48	2.128	Quartz
42.75	2.115	Mullite
50.10	1.82	Quartz



The x-ray diffractogram of the calcined gypsum is presented in Fig. 3.3. This material has impurities upto about 5 % .

3.3 Methods

3.3.1 Production of fly ash - lime - gypsum (FLG) cement

FLG cement is a ground blend of fly ash, lime and calcined gypsum in suitable proportions which on hydration yields strengths rendering a totally water - impervious hard matrix. In the present work fly ash to lime was taken as 2:1 as several of the earlier workers indicated that this ratio yields comparatively better strength. FLG cement of four compositions was prepared by mixing fly ash - lime (2:1) with 5 %, 10 %, 15 % and 20 % respectively of calcined gypsum in a ball mill for about 24 hours. The x-ray diffractogram of FLG cement having 20 % calcined gypsum is indicated in Fig. 3.4.

3.3.2 Specimen preparation

To facilitate a systematic study of the role of different additives individually as well as in combination with each other, hydrated specimens of FLG cement as well as of soil- FLG cement combinations were prepared. For cement hydration, water cement ratio chosen was equivalent to optimum moisture content of soil.

(Fly ash+Lime) : Calcined gypsum = 4:1

Fly ash : Lime = 2:1

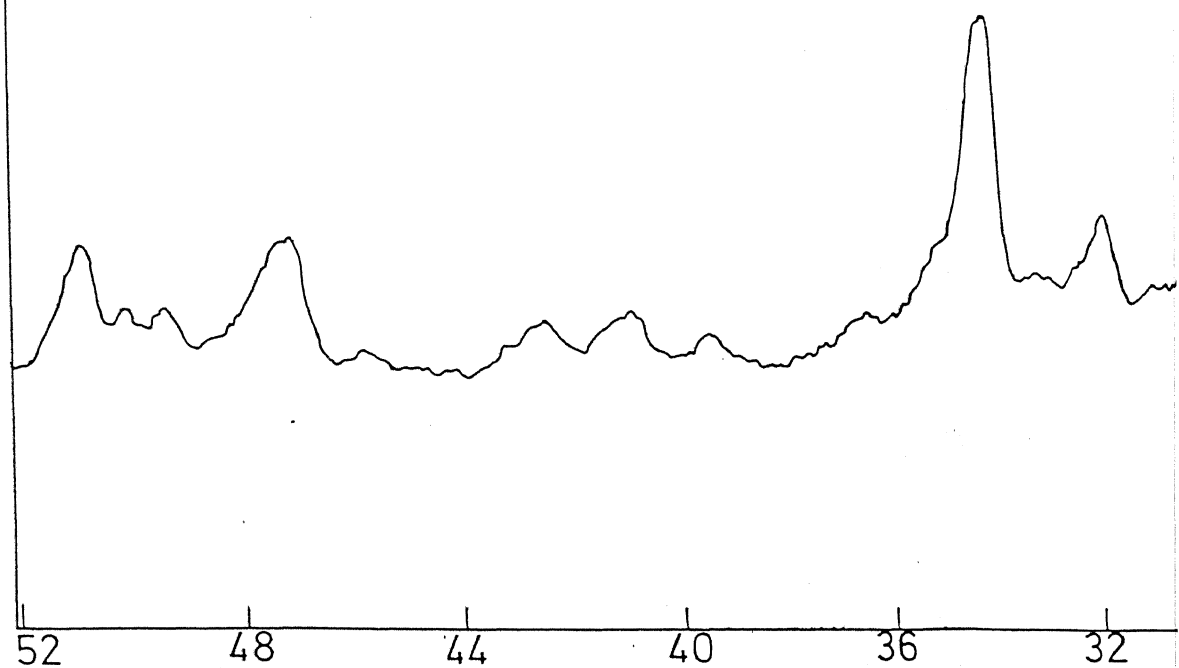
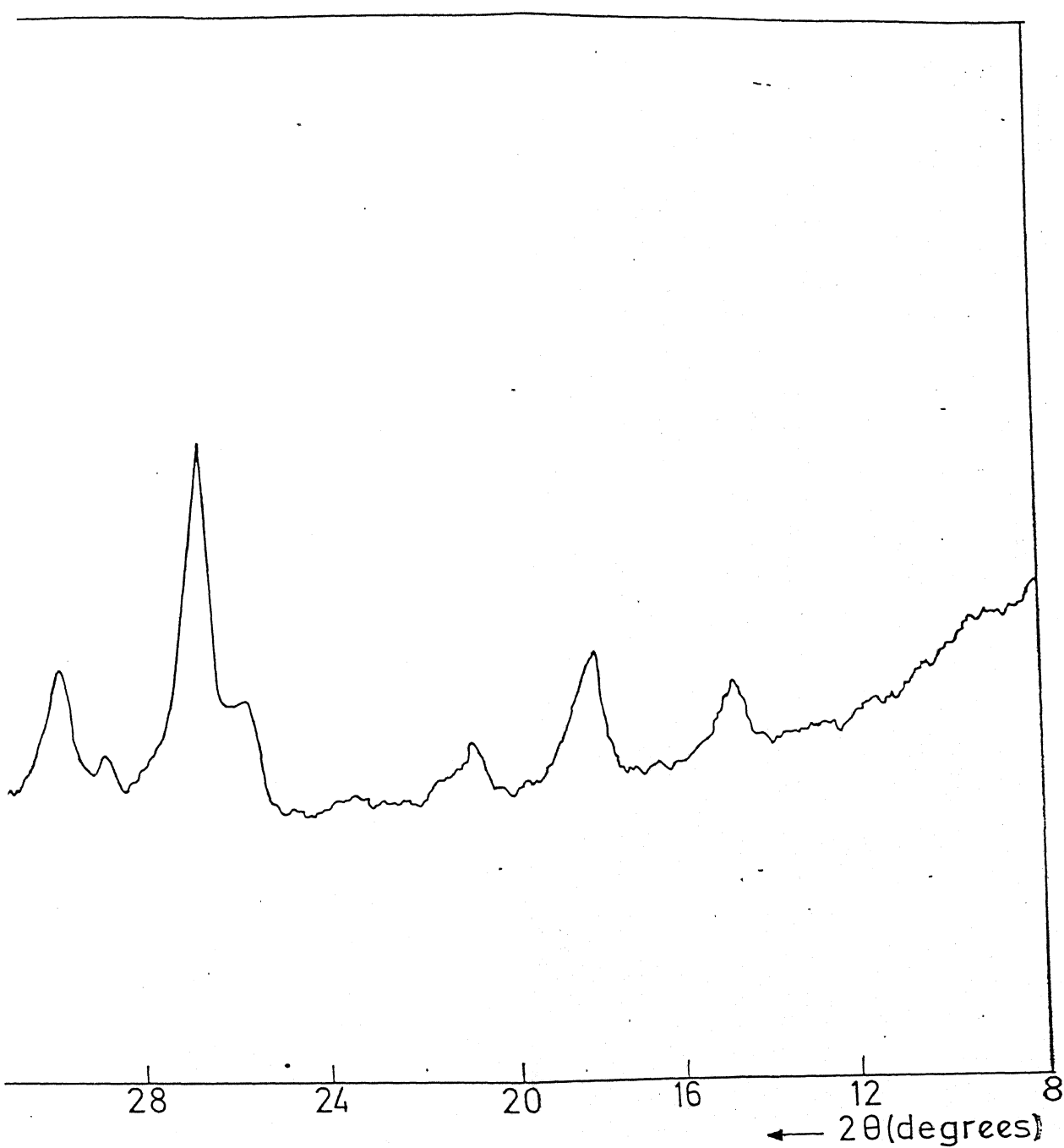


Fig 3.4 X-ray diffractogram
(Radiation used)



am of FLG cement
sed: $\text{CuK}\alpha$)

In soil - FLG cement system, specimens were prepared by thoroughly mixing FLG cement of that composition which has given maximum strength with soil in amounts equal to 4 %, 8 %, 12 %, 16 % and 20 % of the dry weight of soil with moisture equivalent to optimum moisture content of individual mixture determined using the standard Proctor test. After a thorough mixing, the material was compacted in three equal layers using the Harvard miniature compactor mould. The compaction was carried out 25 times over the entire cross section uniformly with the standard specification of the mould. Specimens (of 38.1 mm diameter and 76.2 mm height) were kept in polythene bags to prevent carbonation of cement and also any possible evaporation of the moisture during ageing of the specimens.

3.3.3 Determination of standard consistency and compressive strength of FLG cement

The standard consistency of cement paste was determined using Vicat apparatus at room temperature (about 26° C). It is the amount of water expressed as percentage by mass of the dry cement which permits the Vicat plunger (of 10 mm diameter and 50 mm length) to penetrate to a height 5 to 7 mm from the bottom of the Vicat mould.

The compressive strength of the cement mortar cubes was determined by universal testing machine after 3 days of their curing. The cube mould for this compression test has 70.5 mm side (about 5000 mm² face).

3.3.4 Determination of unconfined compressive strength of soil - FLG cement specimens

Strength tests were carried out on a strain - controlled testing machine. The load was monitored through a proving ring (1300 divisions corresponding to 250 kg) and deformation measured with the help of dial gauge. Loading rate was maintained at 1.270 mm/minute. Different specimens were tested for unconfined compressive strength after 0.5 hr., 3 days, 7 days, 14 days and 28 days of their ageing.

3.3.5 Measurement of pH values

Measurement of pH of all the hydrated specimens of FLG cement and soil - FLG cement system was carried out using a pH meter of SYSTRONIC make (Digital pH Meter 335) fitted with a glass electrode. For this purpose, 20 gms of sample was dispersed in 100 ml of distilled water, stirred for 5 minutes and then filtered before measuring the pH.

3.3.6 X-ray diffraction studies

X-ray diffraction technique was used to determine the mineralogical composition of soil, fly ash, lime and calcined gypsum as well as to track the mineralogical changes in different hydration systems on ageing. Investigations were carried out on x-ray unit of RICH SEIFER make (Model MZ III) using CuK_{α} radiation and Ni filter. The specimens were scanned between 8° and 52° (2θ) using a scanning speed of 3° /minute and a chart speed of 30 mm/minute.

3.3.7 Electron microscopic investigations

Scanning electron microscope of model JEOL JSM - 840 was used to track the morphological features and growth patterns of the cementitious products in hydrated FLG cement and soil - FLG cement system with ageing. This unit has a fully automatic vacuum control system. The operating vacuum is attained through a pumping system controlled by a key. The specimen replacement is accomplished with a comprehensive system of air locks. Specimens were viewed under magnification upto 3×10^5 . The equipment is fitted with an excellent photographic recording facility along with computer which analyzes the composition and also enables detailed x-ray mapping of the individual locations.

Specimen preparation needs to be done with care. The specimen is coated with graphite and later with silver under a vacuum of 0.09 torr. In the present work, carbon coater of Polaron make was used for this purpose. Carbon coating ensures electrical conductivity across those areas of the specimen surface not covered by the subsequent metal coat.

CHAPTER 4

X - RAY DIFFRACTION STUDIES

4.1 General

X-ray diffraction analysis serves as an effective tool for identification of individual mineral constituents in a system. It is extremely beneficial for studying the nature and rate of formation of reaction products in the system such as hydrated FLG cement and soil stabilized with FLG cement on ageing. Some of the compounds, being metastable in nature, might modify with time to stable phases. An understanding of such changes with time is very easily possible with x-ray diffraction analysis. A conventional chemical analysis on the other hand would only provide the proportion of different chemical constituents and hence the overall chemical composition of the system.

In the present chapter, mineralogical changes in hydrated samples of FLG cement and FLG cement - stabilized soil samples during ageing as inferred from the x-ray diffraction data are presented.

4.2 Changes in Hydrated FLG Cement

The x-ray diffractograms (Fig. 4.1) of hydrated samples of cement after ageing of 3 days revealed the formation of

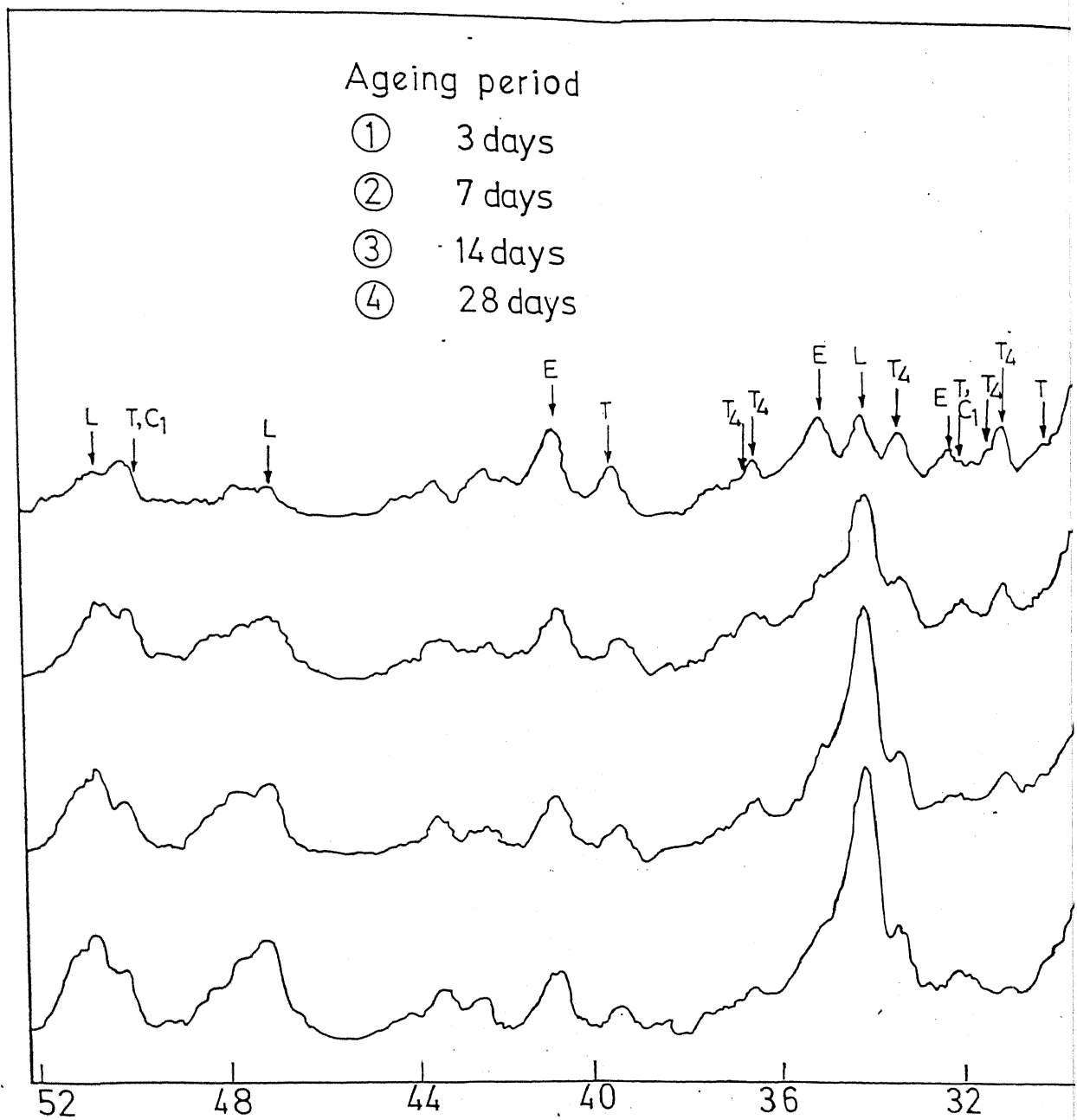
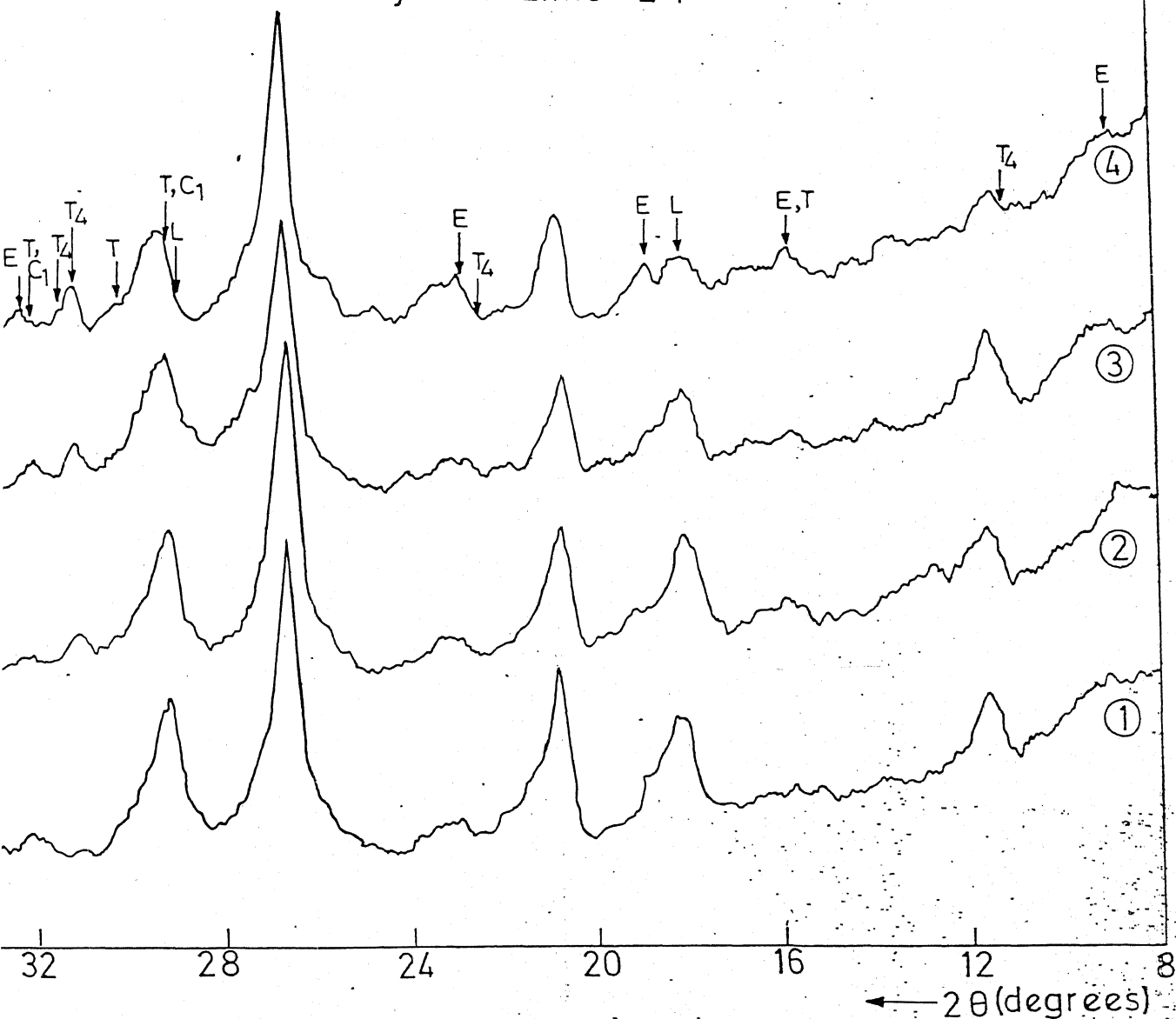


Fig.4.1 X-ray diffractograms on ageing. (Radiation

(Fly ash+Lime): Calcined gypsum = 4:1
 Fly ash: Lime = 2:1



ograms of hydrated FLG cement samples
 Radiation used: $\text{CuK}\alpha$

ettringite ($C_3A \cdot 3CaSO_4 \cdot 32H_2O$)* and tetracalcium aluminate 13-hydrate (C_4AH_{13}), developed as a result of the chemical reaction within the system. Ettringite is identified from its characteristic peaks around 9.73\AA , 5.61\AA , 4.69\AA , 3.88\AA , 2.773\AA , 2.564\AA and 2.209\AA while tetracalcium aluminate 13-hydrate is recognized from its typical peaks at 7.9\AA , 3.95\AA , 2.88\AA , 2.86\AA , 2.69\AA , 2.47\AA and 2.45\AA . Further, a decreasing trend for intensity of peaks of lime [$Ca(OH)_2$] was noticed, indicative of the participation of lime in the formation of these products. Rate of consumption of lime, however was somewhat less upto an initial period of 7 days as observed from minor change in the intensities of its peaks in the x-ray patterns of the specimens aged to 7 days. A drastic reduction in the intensities of the peaks for lime in specimens aged upto 28 days was observed. Presence of 11\AA tobermorite [$Ca_5(Si_6O_{18}H_2) \cdot 4H_2O$] and calcium silicate hydrate ($0.8-1.5 CaO \cdot SiO_2 \cdot 0.5-2.5H_2O$)** after 7 days was confirmed on the basis of their characteristic peaks. Both these compounds improved in their crystallinity with time of ageing. It may be noted here that the compounds that have formed on ageing namely ettringite, tetracalcium aluminate 13 - hydrate, tobermorite and calcium silicate hydrate involved a substantial

* In cement chemistry, different abbreviations are used for different oxides, such as C = CaO, A = Al_2O_3 , S = SiO_2 and H = H_2O .

** Denoted by CSHI.

participation of calcium oxide (CaO) which is the essential ingredient of lime. Contribution of silica and alumina was from fly ash as confirmed from the reduction in the intensities of silica and alumina peaks in the x-ray patterns concomitant with the improvement in the intensities of the peaks for cementitious products.

As for the products formed during ageing while ettringite was the only product present in the very initial period of ageing, the calcium silicate hydrate and aluminate hydrate species developed during the latter part of the ageing periods during which time, the rate of formation of ettringite has substantially diminished.

4.3 Changes in Soil - FLG Cement System

To track the mineralogical changes responsible for strength development in soil - FLG cement stabilization and also the role of clay minerals of soil in stabilization, systematic x-ray diffraction investigations were carried out.

The x-ray diffractograms (Figs. 4.2 to 4.6) of soil stabilized with cement revealed that muscovite and iron minerals such as hematite ($\alpha\text{-Fe}_2\text{O}_3$) and lepidocrocite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) present in the soil have either not participated or participated to the minimum extent in the chemical reaction as confirmed from the absence of any modifications in the intensities of their characteristic peaks. But aluminium minerals such as α -alumina ($\alpha\text{-Al}_2\text{O}_3$), gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) and the clay mineral kaolinite present in the

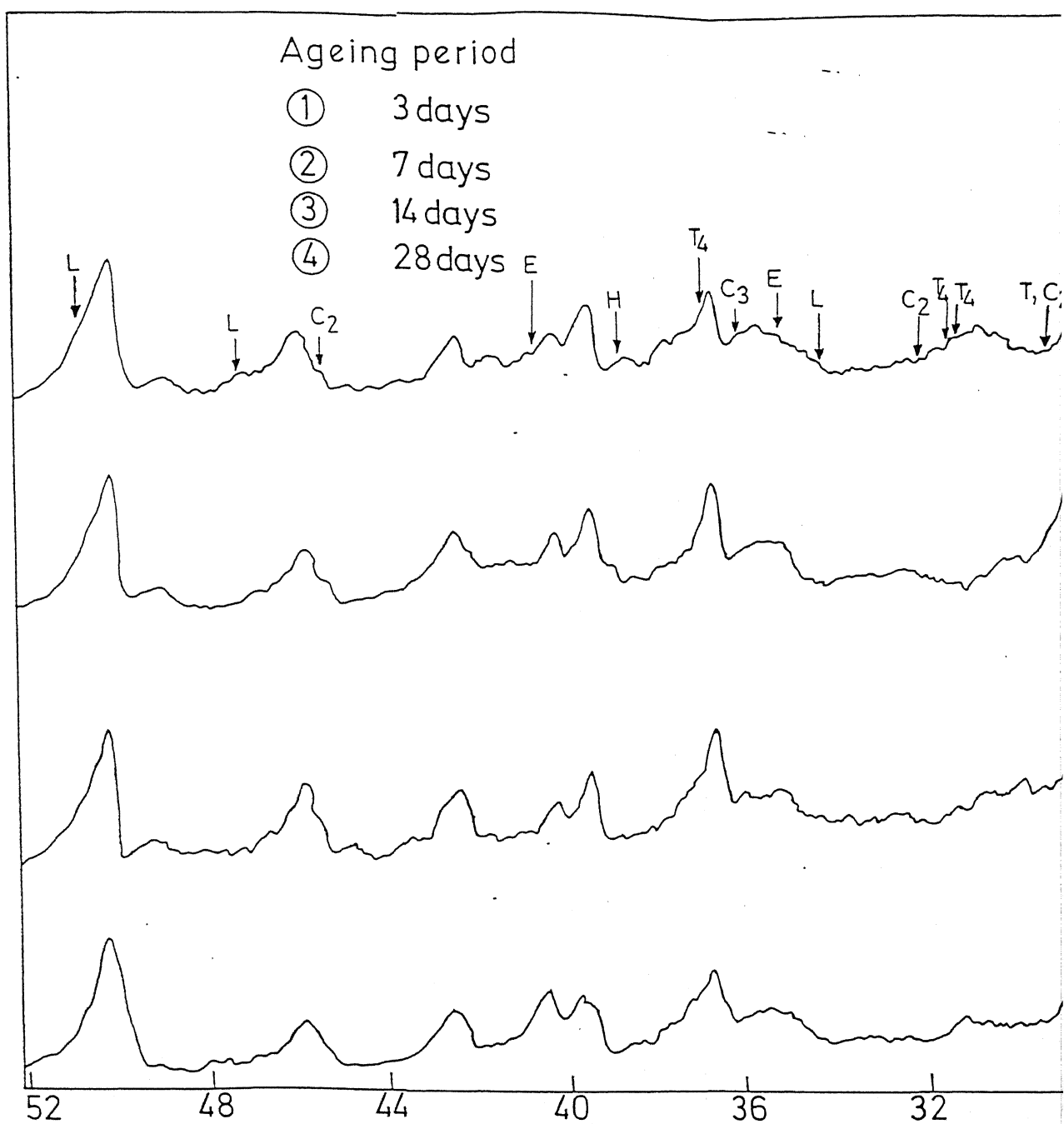
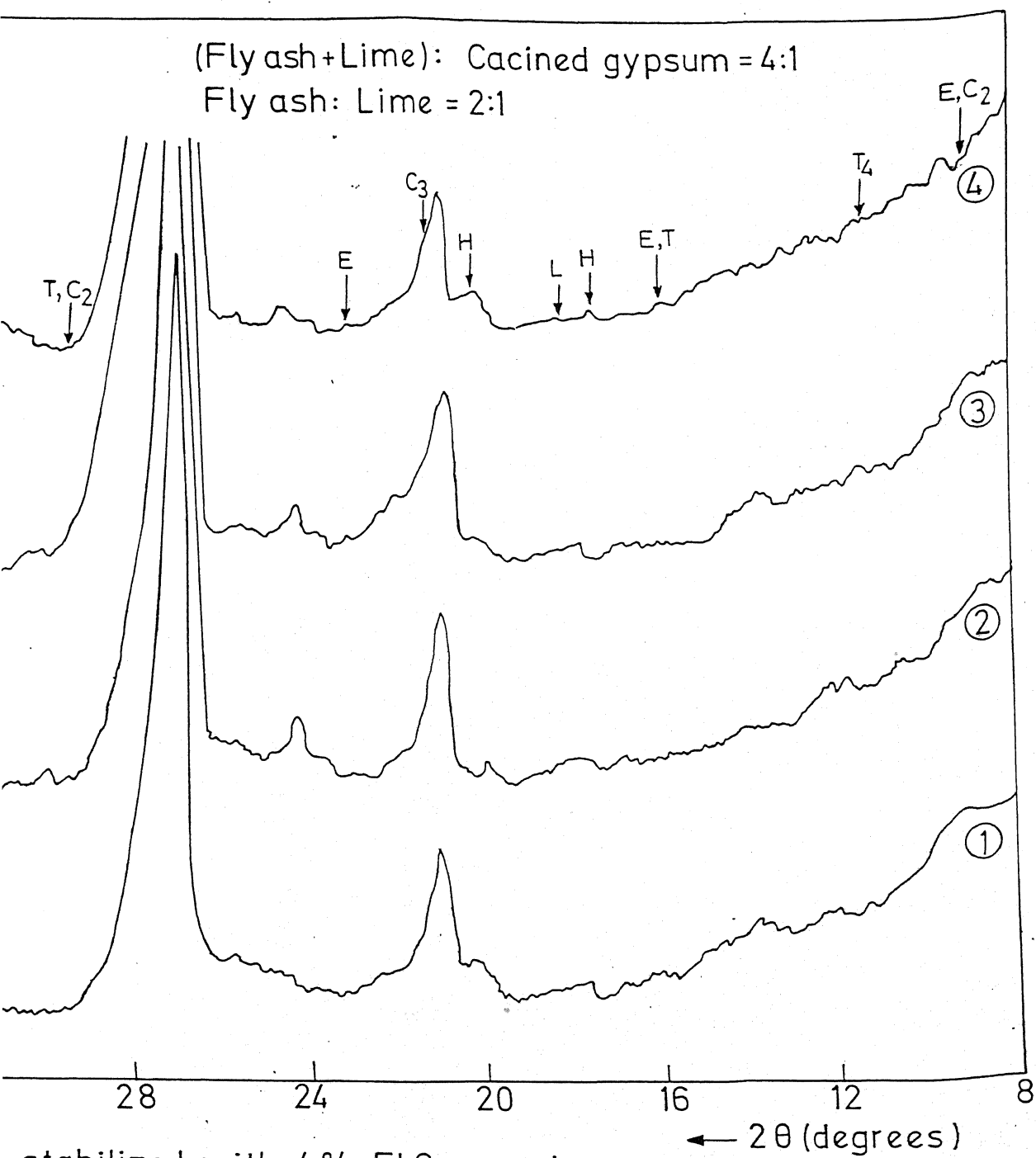


Fig. 4.2 X-ray diffractograms of soil state
(Radiation used:

(Fly ash+Lime): Cacicined gypsum = 4:1

Fly ash: Lime = 2:1



stabilized with 4% FLG cement
(ed: $CuK\alpha$)

Ageing period

- ① 3 days
- ② 7 days
- ③ 14 days
- ④ 28 days

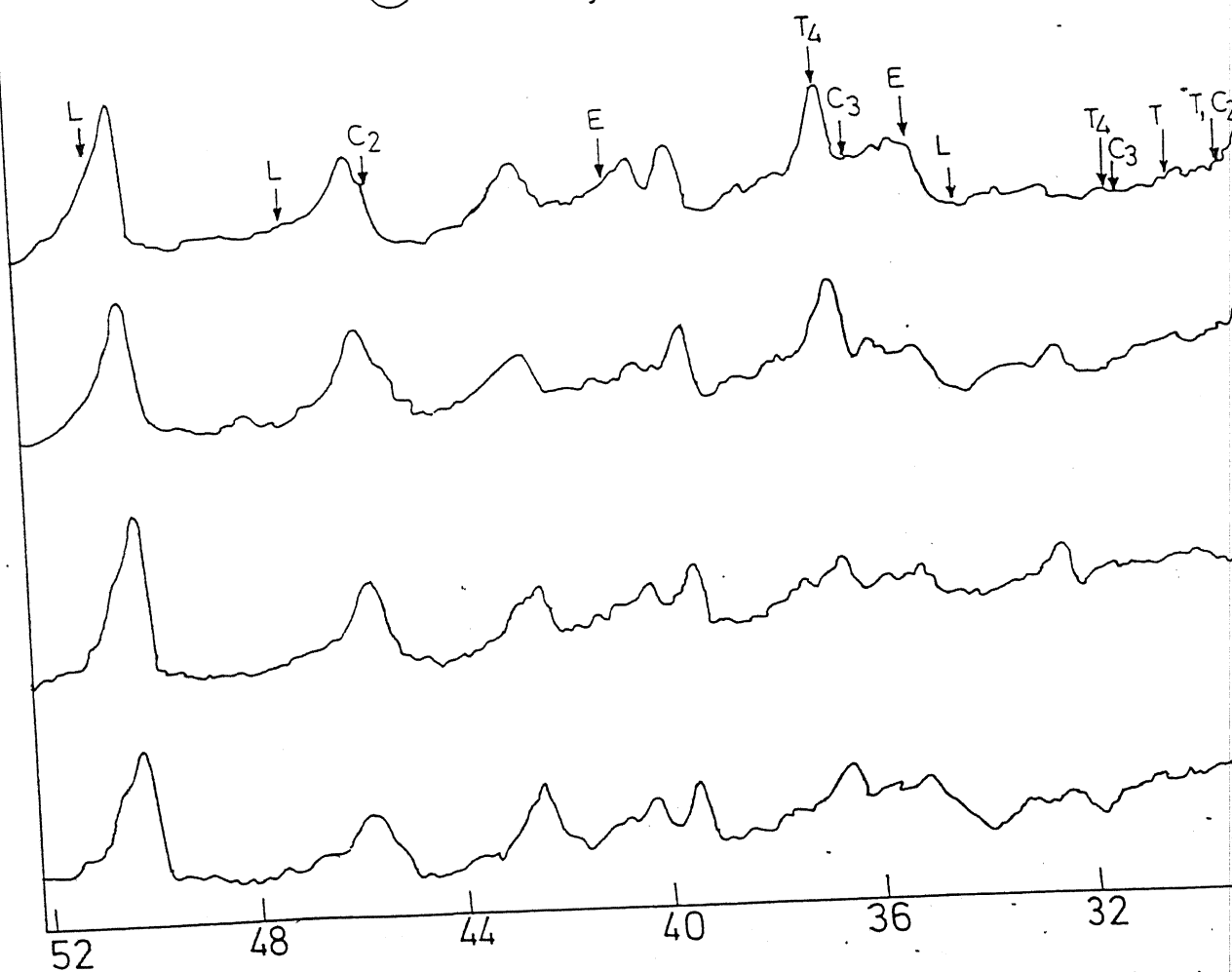
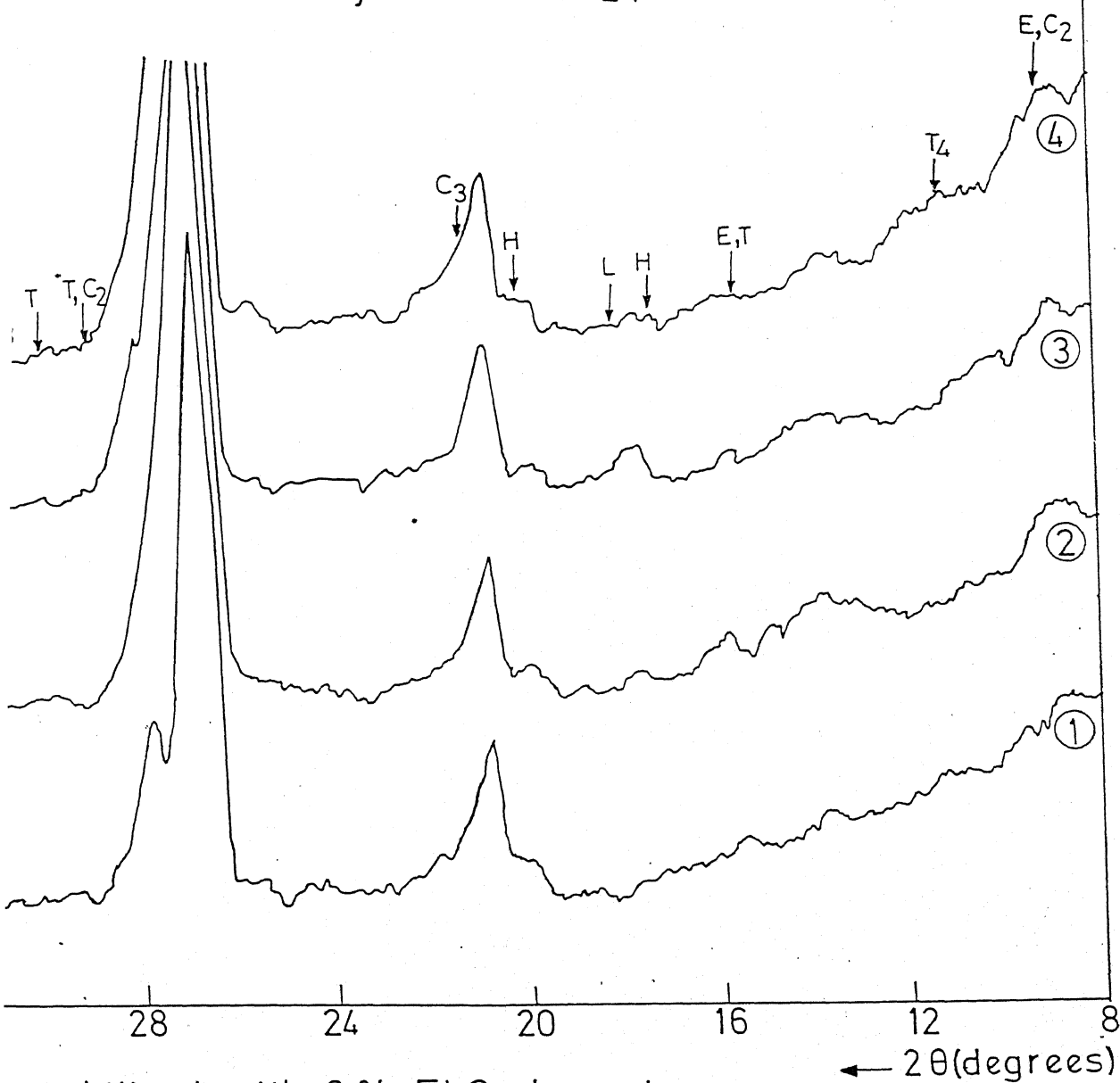


Fig.4.3. X-ray diffractograms of soil sta
(Radiation used:

(Fly ash + Lime): Calcined gypsum = 4:1

Fly ash : Lime = 2:1



stabilized with 8% FLG element
sed: $CuK\alpha$)

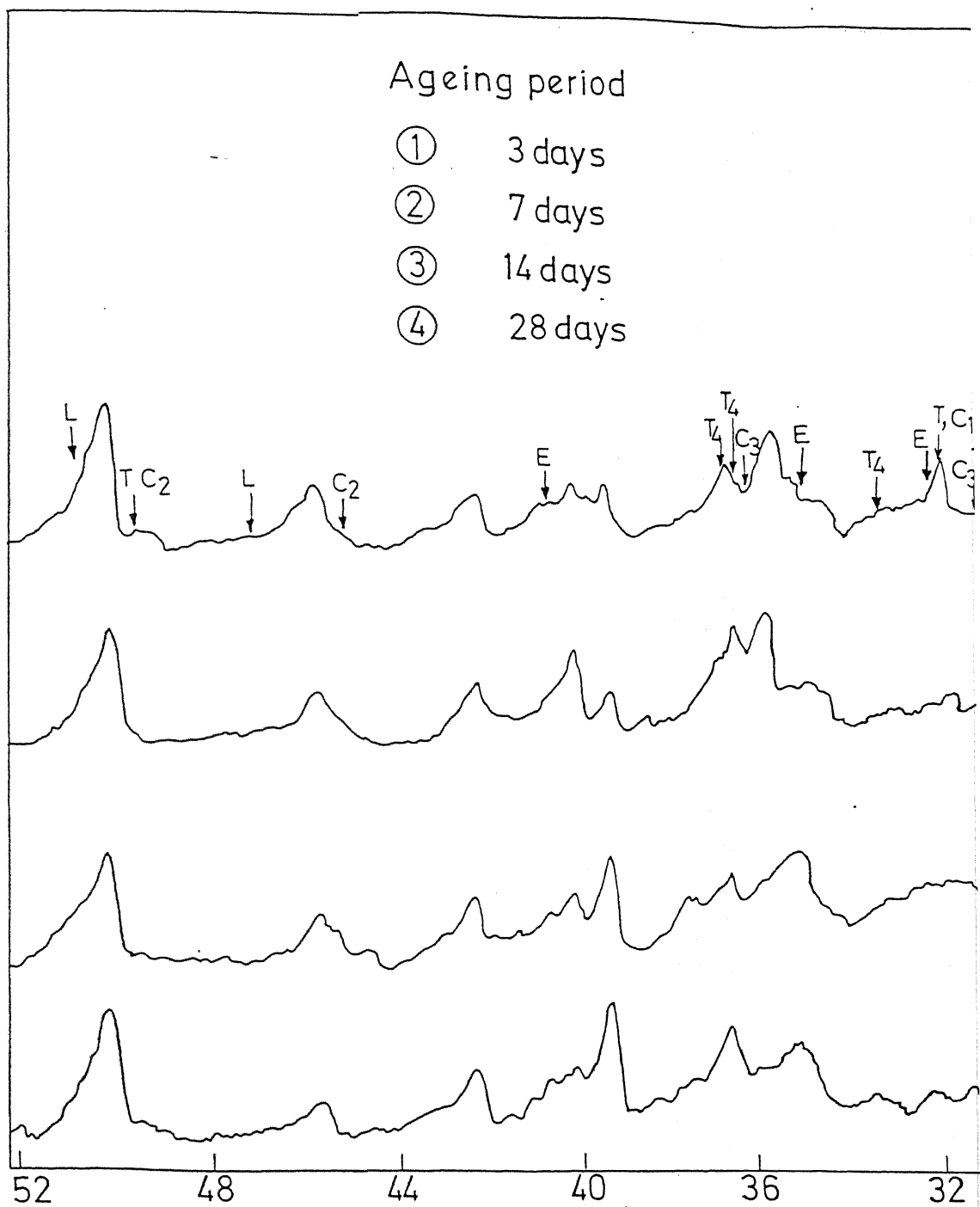
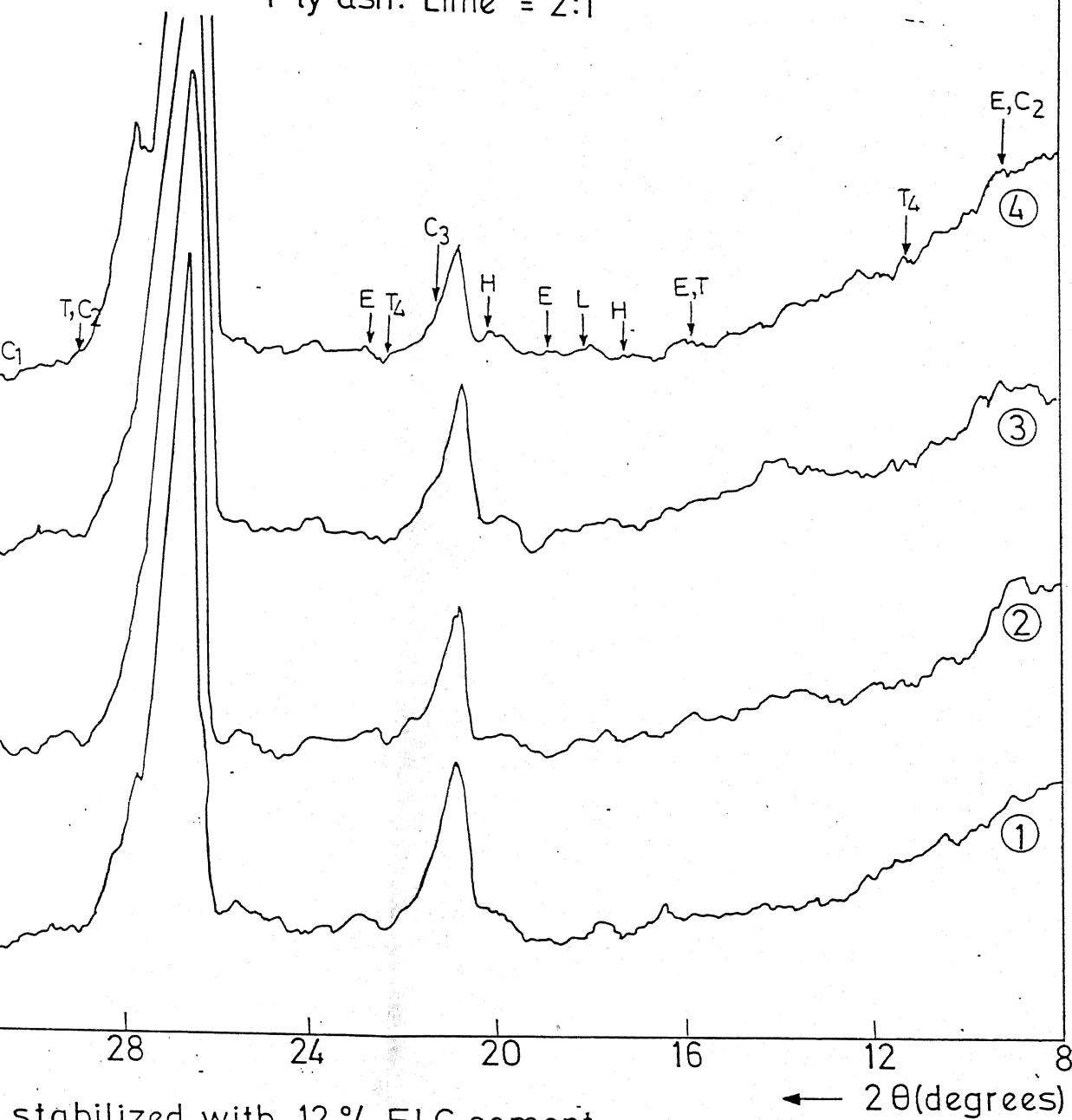


Fig.4.4 X-ray diffractograms of soil
(Radiation u

(Fly ash+Lime): Calcined gypsum = 4:1

Fly ash: Lime = 2:1



stabilized with 12 % FLG cement
(CuK_{α})

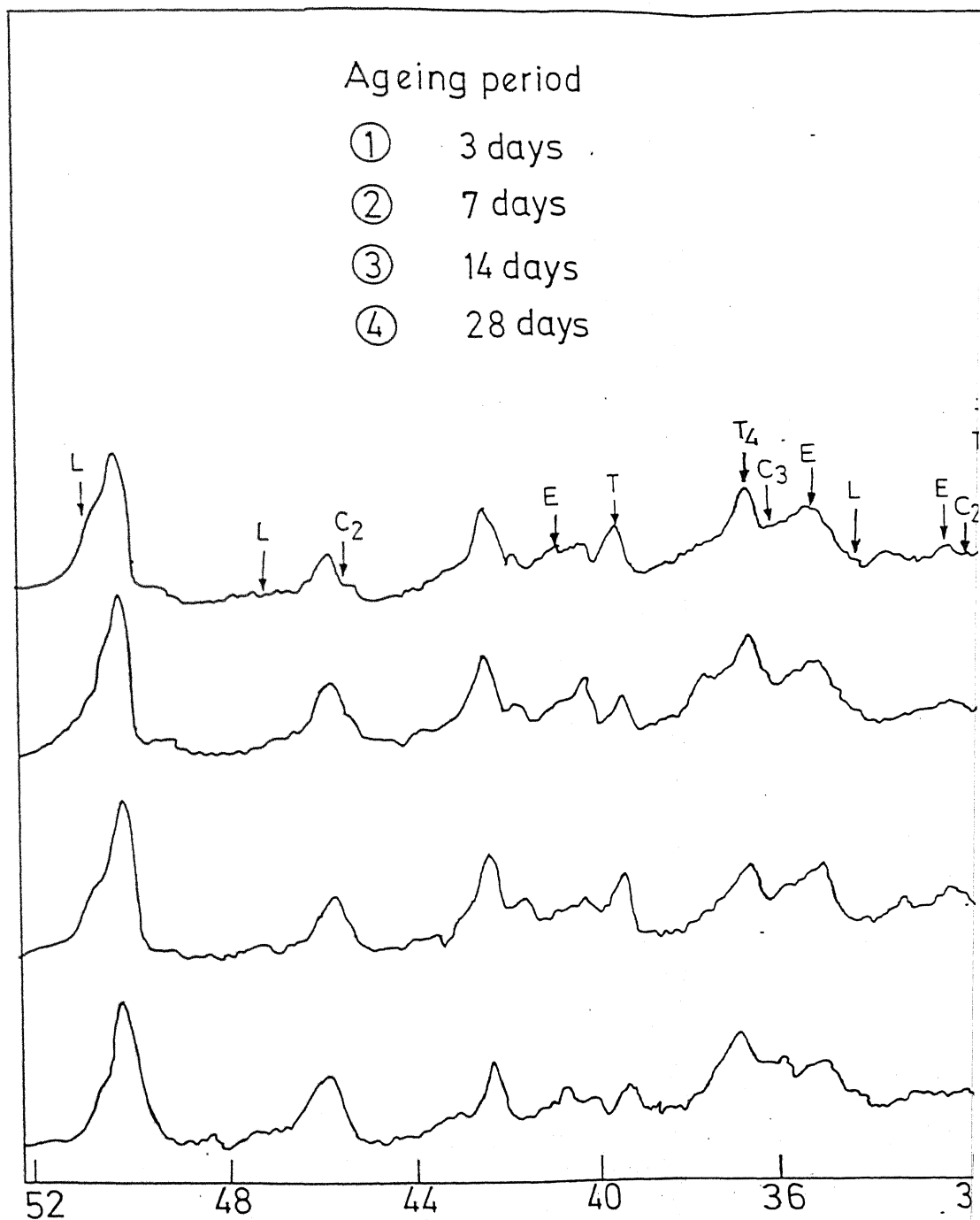
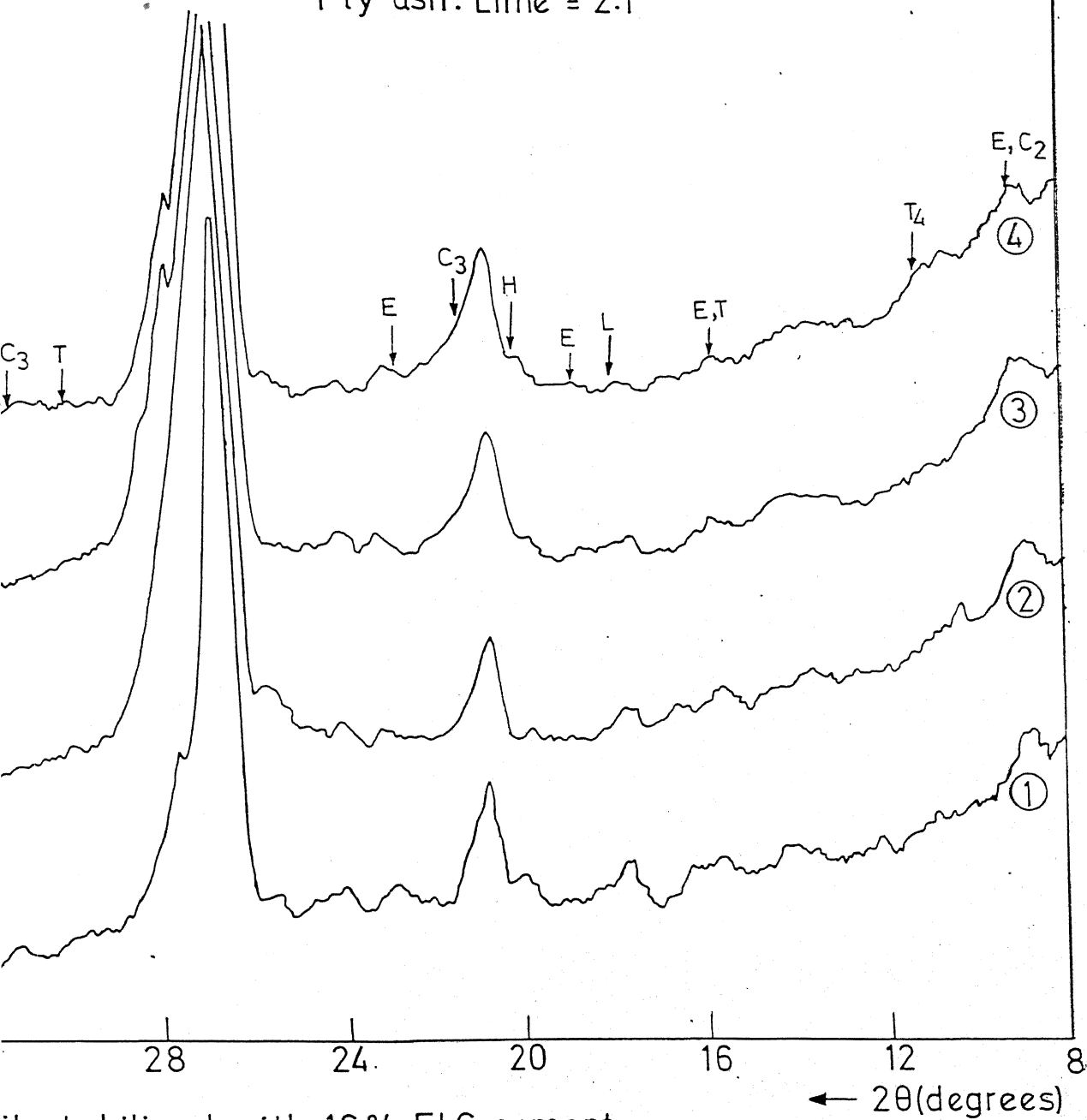


Fig.4.5 X-ray diffractograms of s
(Radiation

(Fly ash+Lime): Calcined gypsum=4:1

Fly ash:Lime = 2:1



il stabilized with 16% FLG cement
used: CuK_{α}

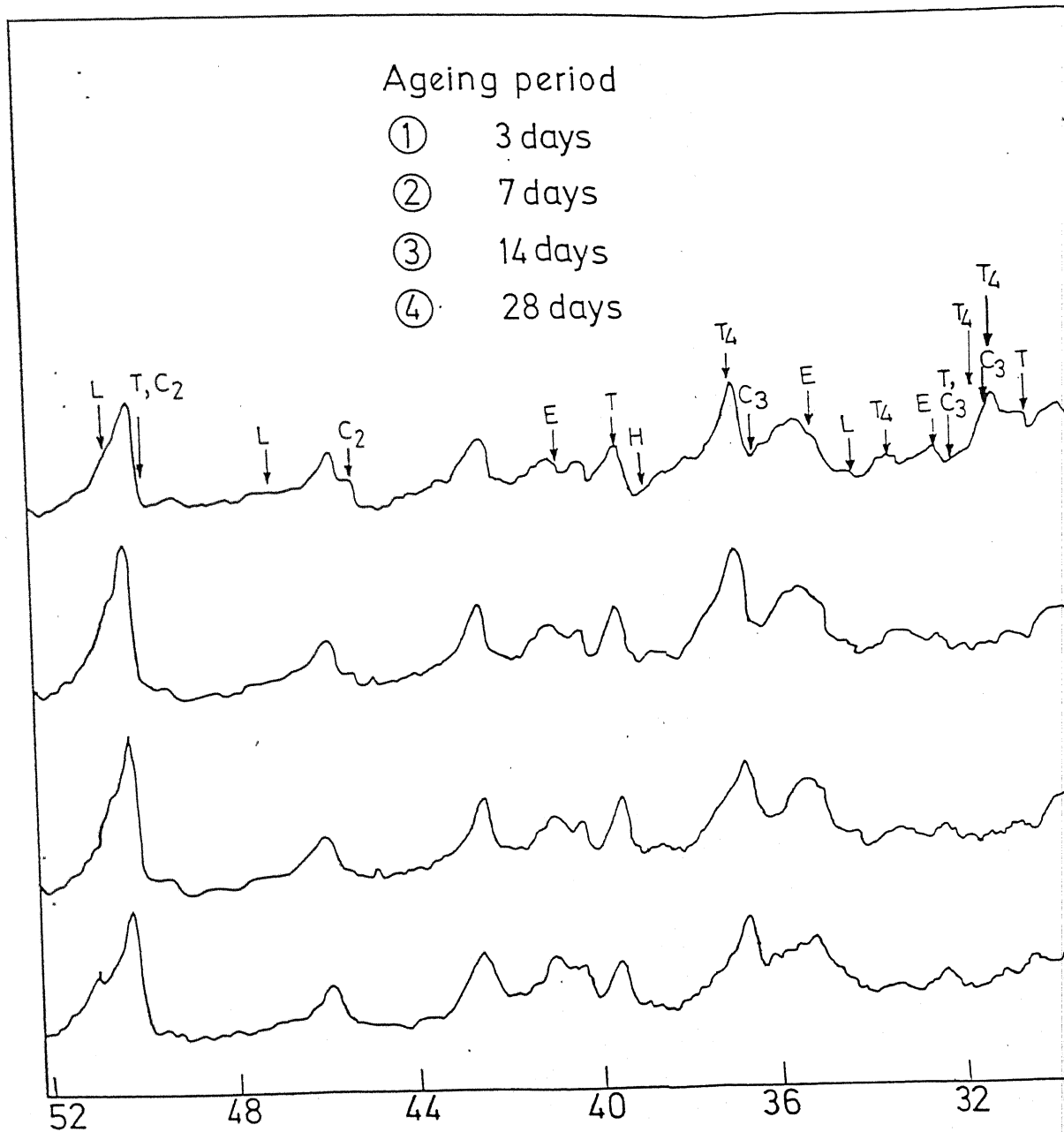
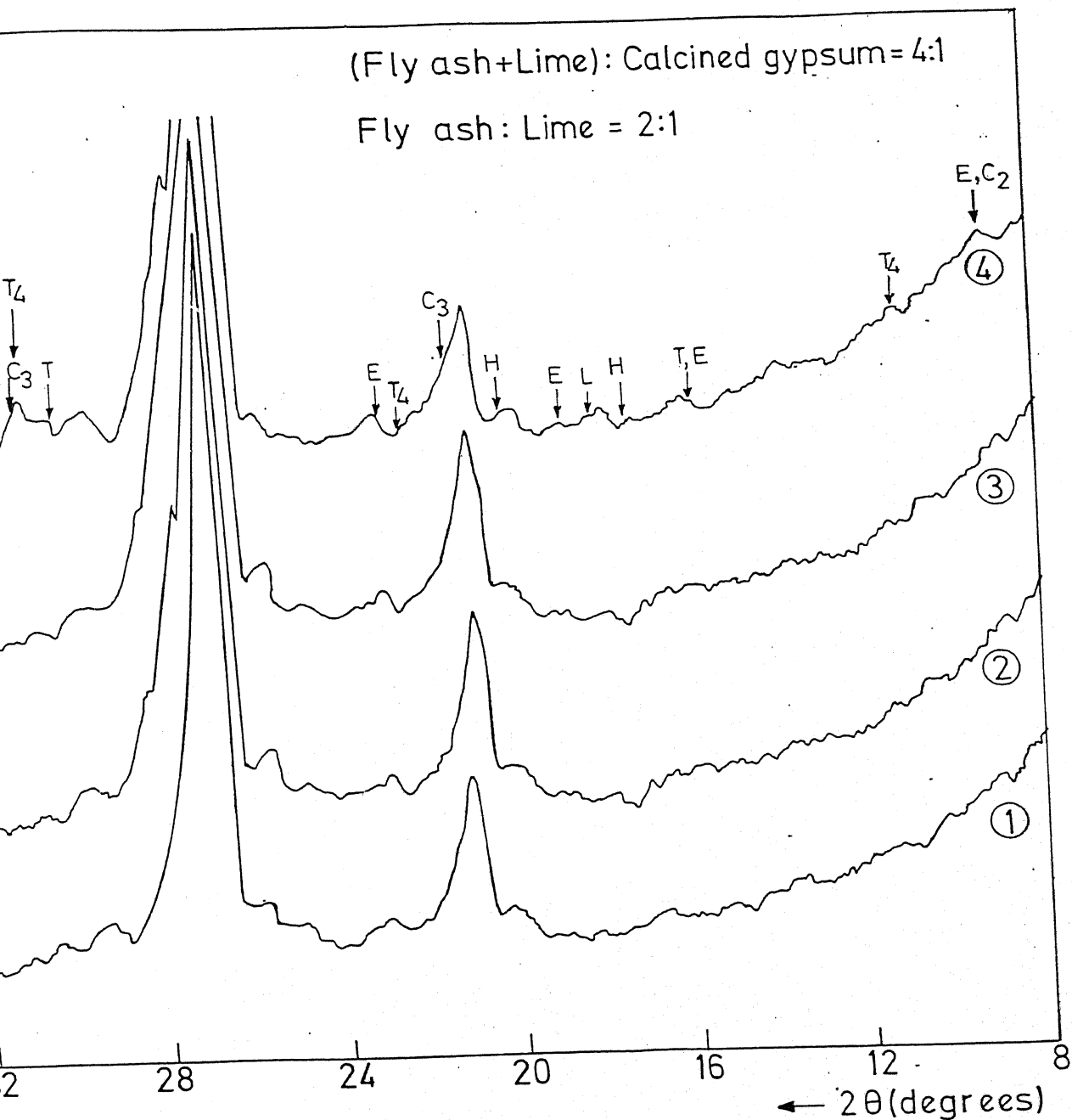


Fig. 4-6 X-ray diffractograms of s
(Radiation u



of soil stabilized with 20% FLG element
 tion used: $\text{CuK}\alpha$)

soil have participated in providing alumina (Al_2O_3) and silica (SiO_2) for the formation of cementitious products such as ettringite in the very initial stages of ageing and calcium silicate and aluminate hydrate species during the later part of the ageing period, as observed from the reduction of intensities of their typical peaks.

Compared to the situation in the hydrated FLG cement specimens, the rate of the formations of the cementitious products in the hydrated soil - cement specimens appears to be less. Also the type of calcium silicate hydrate formed during ageing was not same as indicated by absence of 2 \AA peak in hydrated Fal-G cement specimens and presence in hydrated soil-cement specimens. In the former, the calcium silicate hydrate formed was CSHI while in the latter CSHII appears to be the product.

In addition to the compounds described above, formation of hydrogarnet and the Strätling's compound is an interesting feature in the present case. Presence of hydrogarnet as a reaction product was confirmed from its characteristic peaks at 5.11 \AA , 4.40 \AA and 2.318 \AA . With time, this product has improved in its crystallinity and amount. The reduction in the clay peaks with time has further confirmed the contribution of clay in the formation of hydrogarnet. It is to be noted here that the amount of hydrogarnet varies with the percentage of cement in the specimens.

Presence of gehlenite hydrate (also known as Strätling's compound), with a composition of dicalcium aluminate silicate 8-hydrate (C_2ASH_8) was observed during the initial ageing period recognised from its typical peaks at 4.183 Å, 2.873 Å and 2.489 Å. But in later periods, its presence in x-ray diffractogram was not visible, indicating its metastable nature and hence possibly getting converted into a stable species (either into hydrogarnet or ettringite) depending on the percentage of cement present in the system.

CHAPTER 5

ELECTRON MICROSCOPIC INVESTIGATIONS

5.1 General

The studies involved in the characterization and tracking of changes in soils during stabilization can be classified under three categories. While at one end of the studies, the macroscopic investigations such as the strength behaviour exist, on the other extreme, investigations at atomic lattice level are involved as with the x-ray diffraction studies. The wide gap between the changes at the lattice level and the material behaviour at the macroscopic level can be effectively bridged through microscopic studies. In this regard, electron microscopy serves as an effective tool.

It has been established in the previous chapter that different mineralogical changes take place on ageing in hydrated FLG cement and in the soil stabilized with FLG cement. The cementitious products have been identified and their growth patterns monitored on the basis of x-ray diffraction technique.

For a product to be identified in the x-ray pattern, it has to be crystalline and also in sufficient quantity (above the limit of

detection). However, the product initially appears in the gel form or in minor amounts which results often either in a very broad hump or a low intensity peak in the x-ray pattern. In such cases, electron microscope in particular serves as an effective tool in tracking reaction products on ageing. The precise mode of alteration of the different constituents present in the specimens can be established only through electron microscopic study, although the reaction between the lime on different constituents present in the system can be observed by reduction in the intensity of peaks of the contributing materials in x-ray diffractograms.

Electron microscopy has been used as a tool in soil and related investigations in the past (Croft, 1963; Push, 1966; Smart, 1969; Barden and Sides, 1970; Gokhale and Swaminathan, 1983). In the present investigation, scanning facility has been used to arrive at a better understanding of the nature of changes at the particle level, with regard to the mode of formation of the reaction products and their inter-relationship with the starting materials. All the specimens which have been analyzed by x-ray diffraction technique, have been examined under high magnifications using scanning electron microscope.

5.2 Morphology of the Products in Hydrated FLG Cement

As indicated in chapter 4, several mineralogical changes took place in hydrated cement on ageing. In the specimens aged to 3 days, the reaction was not evidenced in the scanning electron

micrograph (SEM). Ettringite observed in the x-ray diffractograms is not clearly observed in the SEM (Fig. 5.1). This points to the fact that this product although present in its initial development stage, however, has not crystallized in typical morphology that could be seen in the SEM.

At the end of 7 days, the reaction was relatively more pronounced. Development of ettringite in the shape of hexagonal grains and fibrous cementitious products could be clearly evidenced (Fig. 5.2).

During the reaction, the alteration of the material appeared to be initiated at the periphery of the grains. Several of the grains of the cement material exhibited the reaction rims at the end of 14 days of ageing (Fig. 5.3). While grains were altered to the calcium silicate hydrate phase, development of tobermorite with characteristic tubular morphology was clearly noticed in the samples aged to 28 days (Figs. 5.4 and 5.5). In addition to the reaction rims (Fig. 5.3), the tubes appeared to grow from the grain boundaries (Figs. 5.4 and 5.5). Initiation of the growth of tobermorite is noticed from the characteristic relief of the grain boundaries (Fig. 5.5).

5.3 Morphology of the Products in Soil-Cement System

Distinction can be made between the cementitious products formed during the initial ageing period and long - term ageing. Short-term strengths, with all clay minerals, are attributed to

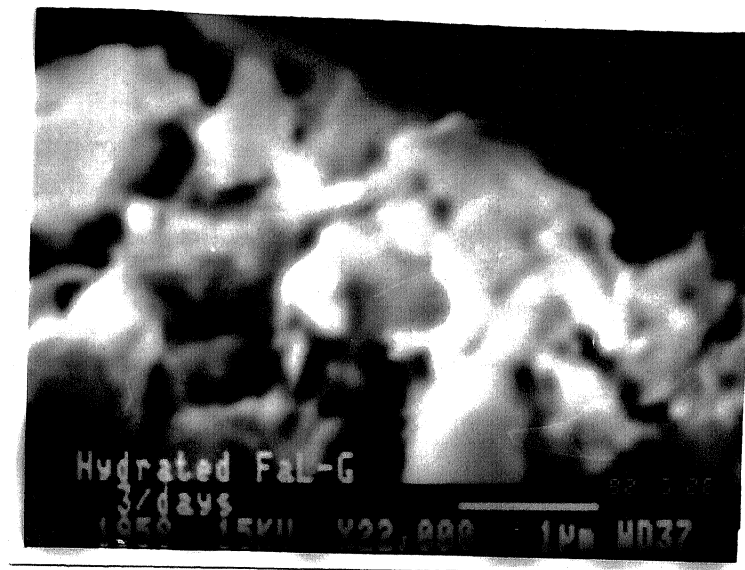


Fig. 5.1 Uniform surface coating without specific crystalline form in the grains of hydrated cement specimen, aged to 3 days (SEM)



Fig. 5.2 Hexagonal grains of ettringite and fibrous cementitious products in the hydrated cement specimen, aged to 7 days (SEM).



Fig. 5.3 Reaction rims in the grains of hydrated cement, aged to 14 days (SEM).

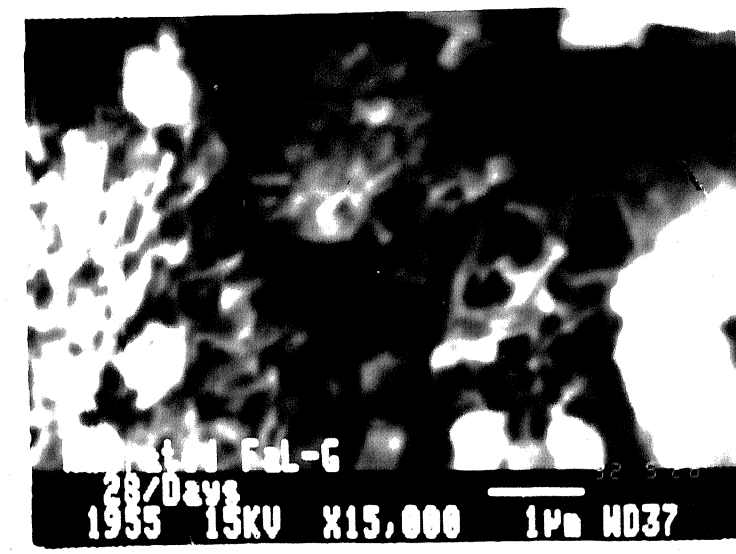


Fig. 5.4 Laths of tobermorite, furred crystals of CSHI and hexagonal plates of C_4AH_{13} in addition to reaction rims in the hydrated cement, aged to 28 days (SEM).

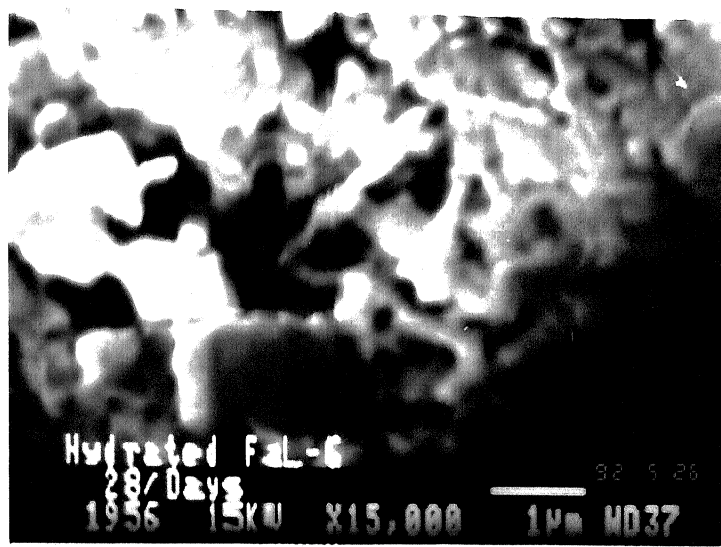


Fig. 5.5 Laths of tobermorite, furlled crystals of CSH I and hexagonal plates of C_4AH_{13} in addition to reaction rims in hydrated cement, aged to 28 days (SEM).

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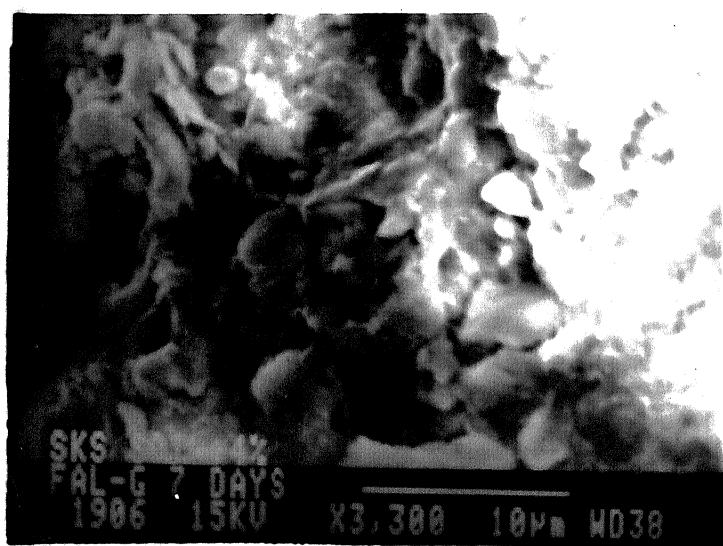


Fig. 5.6 Development of cementitious products by chemical reaction with soil particles in soil stabilized with 4 % cement and aged to 7 days (SEM)

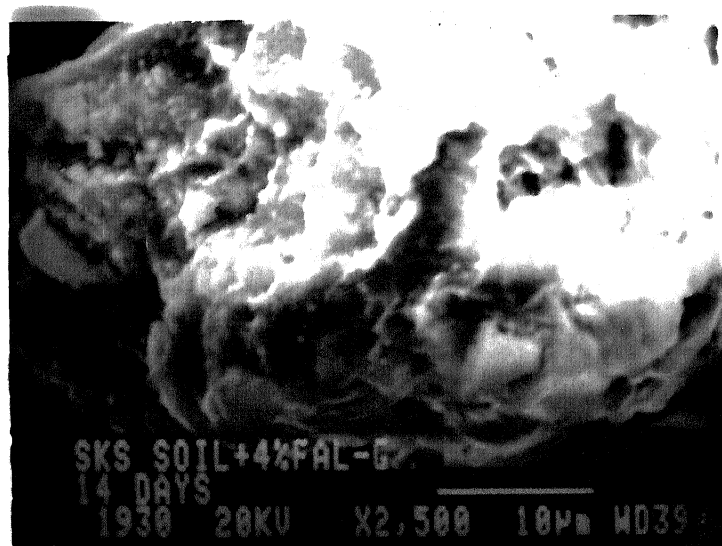


Fig. 5.7 Development of fibre bundles of calcium silicate hydrate (CSHII) along with hexagonal outlines of hydrogarnet and C_4AH_{13} in soil stabilized with 4 % cement and aged to 14 days (SEM).



Fig. 5.8 Development of needles of ettringite in soil stabilized with 8 % cement and aged to 7 days (SEM).

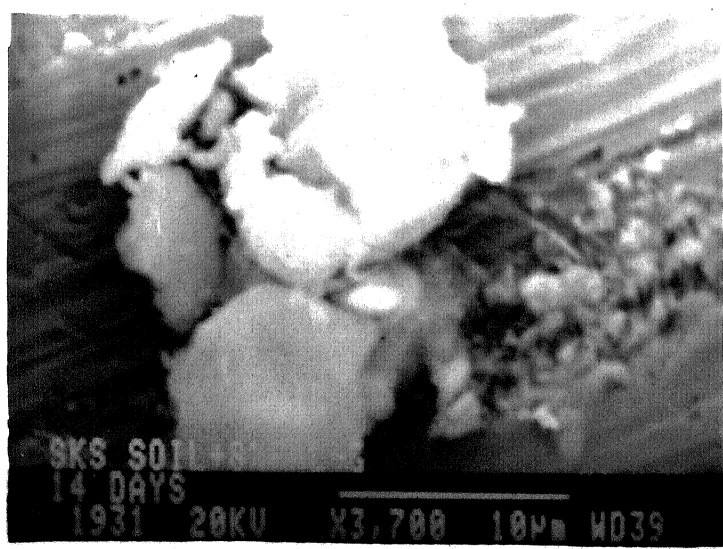


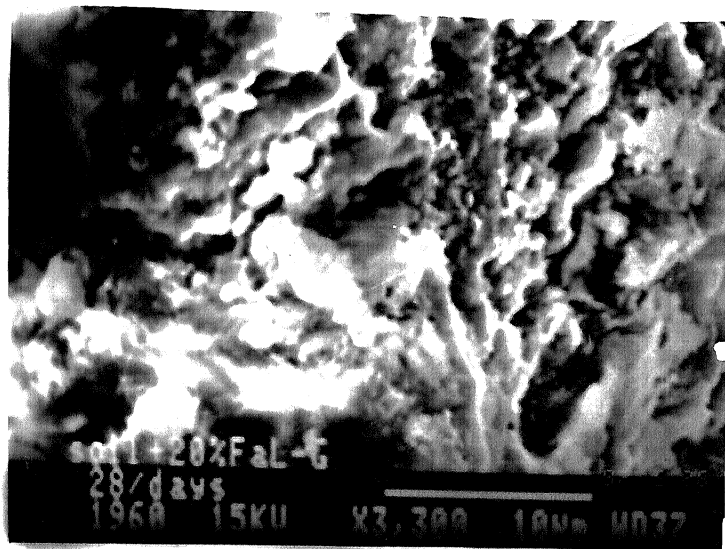
Fig. 5.9 Development of tobermorite laths in soil stabilized with 8 % cement and aged to 14 days (SEM).



Fig. 5.10 Hexagonal morphology of hydrogarnet and calcium aluminate 13 - hydrate exhibited in soil specimen stabilized with 20 % cement and on ageing to 7 days (SEM).



Fig. 5.11 Extensive development of laths of tobermorite and fibre bundles of calcium silicate hydrate (CHSII) in soil stabilized with 20 % cement and aged to 14 days (SEM).



- g. 5.12 Modification of the soil fabric in soil stabilized with 20 % cement and aged to 28 days (SEM).

the formation of mixed gelatinous and poorly "structurally ordered" phases whereas base exchange plays no significant role; while long - term strength is due to gradual crystallization of new mineral species from the gelatinous reaction products (Croft, 1963).

Initial development of cementitious products by chemical reaction with soil particles can be observed in the stabilized soil specimens having 4 % cement and aged to 7 days (Fig 5.6). In the same specimen aged to 14 days, presence of fibre bundles of calcium silicate hydrate (CSHII) along with hexagonal outlines of hydrogarnet and tetracalcium aluminate 13-hydrate (C_4AH_{13}) can be noticed (Fig. 5.7). In the specimens having 8 % cement and aged to 7 days, development of needles of ettringite can be seen (Fig. 5.8). Formation of laths of tobermorite could also be evidenced (Fig. 5.9). Development of hexagonal outlines of hydrogarnet and C_4AH_{13} within the stabilized soil specimens having 20 % cement and aged to 7 days was clearly noticed (Fig. 5.10) alongwith laths of tobermorite and fibre bundles of CSHII (Fig. 5.11). Continued reaction has resulted in distinct modification of the fabric of the specimens (Fig. 5.12).

CHAPTER 6

STRENGTH BEHAVIOUR

6.1 General

The mineralogical changes that occur during the stabilization of soil with FLG cement in presence of water and on ageing upto 28 days, as detailed in the previous two chapters, induce modification in the strength behaviour of the soil. In order to choose the FLG cement of the right composition for use in soil stabilization, initial tests were conducted on cement-sand mortar cubes (cement and sand in the ratio of 1:3). Four different compositions of cement were chosen. On the basis of these tests, the cement of a particular composition was adopted for stabilizing the soil. The strength data for soil-cement stabilized specimens at different periods of ageing were obtained. In the present chapter all the details are provided with explanations for the strength gain in the soil during stabilization.

6.2 Strength Behaviour of Cement Mortar

The determination of standard consistency of cement of different compositions for fixing the quantity of water for the compressive strength test was done. Data obtained (Fig. 6.1)

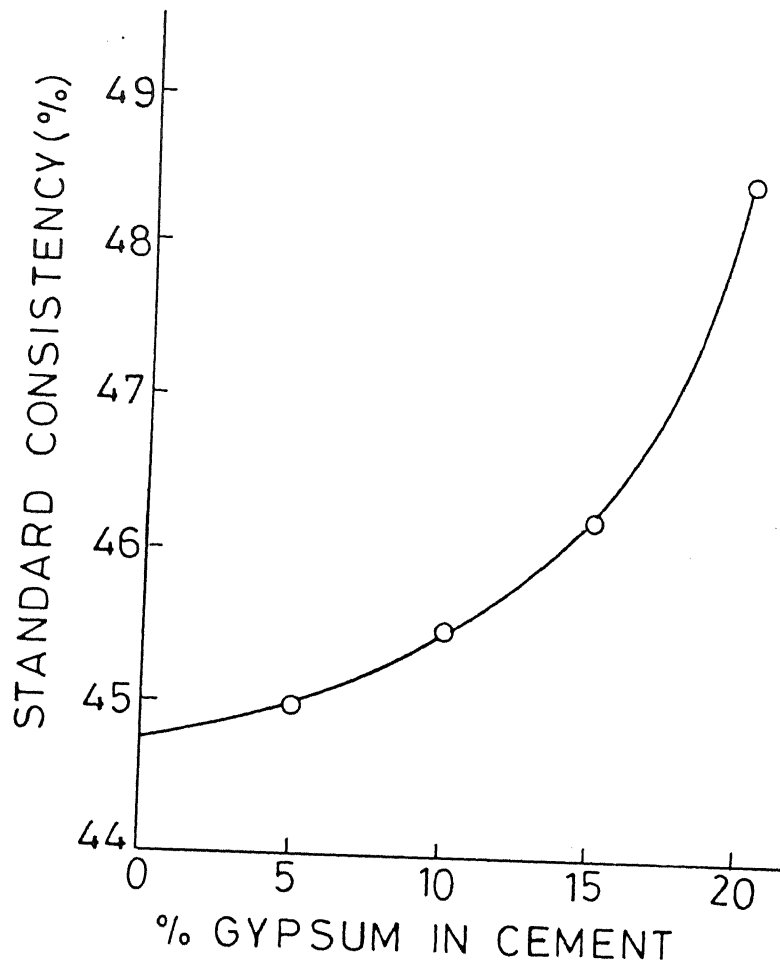


Fig. 6.1 Variation of standard consistency of FLG cement

indicated a general increase of the standard consistency with increasing amount of calcined gypsum [$\text{CaSO}_4 \cdot (0.5)\text{H}_2\text{O}$] in cement. The standard consistency of cement having 20 % calcined gypsum was 48.5 %.

For strength testing, cubes were prepared using cement and standard sand of the following compositions :

gypsum = 5 %, 10 %, 15 %, 20 %

(fly ash + lime) = 95 %, 90 %, 85 %, 80 %

fly ash : lime = 2:1 (in all cases)

cement : sand = 1:3 (in all cases)

For each of the above compositions, three cubes were prepared for testing. All these cubes were cured under water for 3 days prior to testing. It was observed that in the case of cubes having 5 % and 10 % of gypsum, the cubes shape was not retained as grains have dislodged during curing. The bonding was very poor. Hence strength tests could be conducted only on cubes with 15 % and 20 % of gypsum in cement.

The cubes with cement having 20 % gypsum exhibited compressive strength of 0.555 MPa while cubes with cement having 15 % gypsum indicated compressive strength of 0.474 MPa (Table 6.1).

Table 6.1

**Compressive Strength of 1:3 FLG Cement-Sand Mortar Cubes after
3 Days of Curing**

Specimen	Load (N)				Area (sq.mm)	Compressive Strength (MPa)
	1	2	3	Average		
1.Cement having 15 % gypsum	2400	2205	2450	2368.33	5000	0.474
2.Cement having 20 % gypsum	2940	2695	2495	2776.67	5000	0.555

The x - ray diffraction data of hydrated cement having 20 % gypsum during the ageing upto 28 days revealed that ettringite, the dominant product formed in the first 3 days of ageing period, was responsible for the early strength. The sharp reduction in the peaks of lime $[\text{Ca}(\text{OH})_2]$ after initial 7 days of ageing period revealed its involvement in the chemical reaction. Production of cementitious products such as tetracalcium aluminate 13-hydrate $(\text{C}_4\text{AH}_{13})$, 11 Å tobermorite $[\text{Ca}_5(\text{Si}_6\text{O}_{18}\text{H}_2) \cdot 4\text{H}_2\text{O}]$ and calcium silicate hydrate (CSH) were responsible for later strength.

6.3 Strength Behaviour of Stabilized Soil-Cement System

Unconfined compressive strength (U.C.S.) values of soil specimens stabilized with 4 %, 12 %, 16 % and 20 % cement having

20 % gypsum respectively are given in Table 6.2 and their variations are indicated in Fig. 6.2. The U.C.S. of the soil specimen at its optimum moisture content was 0.038 MPa. The specimens prepared with cement have registered an improvement as can be seen from Table 6.2 and Fig. 6.2.

Table 6.2

Unconfined Compressive Strength Values (MPa) for Soil-Cement Specimens on Ageing.

Specimen	Fresh	3 days	7 days	14 days	28 days
Soil+4 % Cement	0.039	0.045	0.047	0.065	0.131
Soil+8 % Cement	0.041	0.148	0.183	0.203	0.231
Soil+12 % Cement	0.046	0.160	0.194	0.338	0.580
Soil+16 % Cement	0.049	0.198	0.318	0.439	0.644
Soil+20 % Cement	0.052	0.221	0.406	0.520	0.869

Distinct trends could be noticed in the strength development. In the case of soil samples stabilized with 4 % and 8 % cement, strength enhancement was mostly during the initial 7 days of ageing. On the other hand the strength gain during this period in the case of soil samples with increasing cement was relatively low compared to the later period. Ettringite and tetracalcium aluminate 13-hydrate (C_4AH_{13}) which form in the very early period of ageing contributed the early strength, whereas on 28 days of ageing 11 Å tobermorite, calcium silicate hydrate

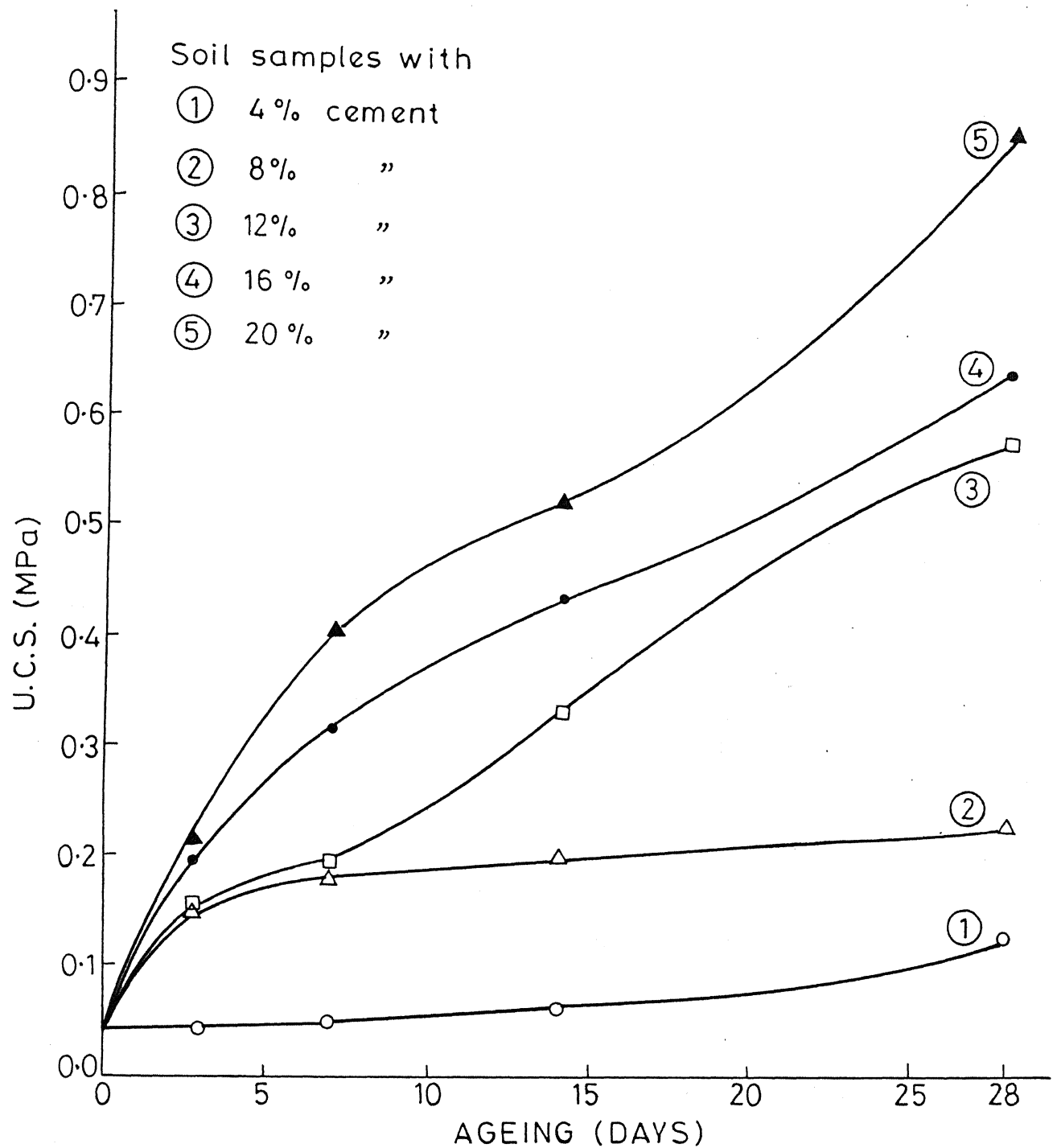


Fig.6-2 Unconfined compressive strength variations in soil stabilized with FLG cement.

[Cement composition -(Fly ash + Lime): gypsum = 4:1 and Fly ash : Lime = 2:1]

(CSHII) and hydrogarnet formed as the reaction products were responsible for later strength gain. The continued increase in strength in later cases can be relagated to the increased participation of cement with increased quantity of gypsum. As indicated in the previous chapter (chapter 4), gehlenite hydrate (Stratling's compound) is the product with increase of gypsum which is converted into ettringite and hydrogarnet depending on the percentage of cement mixed in the soil specimens. From x-ray diffraction data it was observed that hydrogarnet was more in amount in soil specimens having low percentage of cement and so it was responsible for latter strength. But in case specimens with higher percentage of cement, the latter strength is mainly due to calcium silicate hydrate (CSHII), tobermorite and calcium aluminate hydrate (C_4AH_{13}).

Table 6.3
pH Values of Soil-Cement Specimens on Ageing

Specimen	Fresh	3 days	7 days	14 days	28 days
Soil+4 % Cement	12.66	12.60	12.40	11.28	10.63
Soil+8 % Cement	13.11	13.09	12.95	11.88	10.98
Soil+12 % Cement	13.13	13.12	12.09	12.00	11.30
Soil+16 % Cement	13.13	13.12	13.02	12.13	11.33
Soil+20 % Cement	13.13	13.12	13.04	12.26	11.57

It is interesting to note that a significant reduction in the pH of the soil-cement system occurred between 7 days and 28 days of ageing (Table 6.3). This reflects to greater silica solubility during this period with consequent formation of the calcium silicate hydrate species.

CHAPTER 7

INTEGRATED PICTURE

Fly ash, a by-product obtained from burning of coal in thermal power plant at Panki (Kanpur), contains about 57 % of silica (SiO_2) and 23 % of alumina (Al_2O_3). In the present study, fly ash in conjunction with lime and gypsum was utilized as the cement material (FLG cement) that was used for the stabilization of red soil. Presence of lime in the system provided the right chemical environment (of high pH) for the formation of cementitious products in the system. To understand the nature of changes during hydration and the rate of each of the additives in soil-cement system with differing compositions, systematic studies were conducted on hydration of cement specimens as well as soil-cement specimens.

The x-ray diffraction studies on hydrated FLG cement specimens have revealed that on initial 3 days of ageing, ettringite ($\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$) is the main product formed followed by the appearance of tetracalcium aluminate 13-hydrate (C_4AH_{13}) on 7 days of ageing. On 28 days of ageing, presence of calcium silicate hydrate (CSH) and tetracalcium aluminate hydrate (C_4AH_{13}) in significant amounts was observed together with 11 Å tobermorite [$\text{Ca}_5(\text{Si}_6\text{O}_{18}\text{H}_2) \cdot 4\text{H}_2\text{O}$] during which time, the rate of

formation of ettringite has substantially diminished. All these cementitious products were also identified in scanning electron micrographs. Taylor (1950) on the basis of experimental investigations reported the formation of CSHI and C_4AH_{13} at room temperature by the reaction of lime with silica sol or gel and water.

FLG cement of four compositions was prepared and tested for compressive strength after three days of curing. Tests on 1:3 cement sand mortar cubes prepared with cement having 20 % calcined gypsum indicated maximum compressive strength (around 0.555 MPa). It is to be noted here that higher value of standard consistency of FLG cement compared to that for Portland cement is indicative of relatively higher water requirement for the chemical reaction to occur in FLG cement.

X-ray diffraction studies of cement stabilized soil at different stages of ageing indicated the formation of gehlenite hydrate (Strätling's compound, C_2ASH_8) and hydrogarnet in addition to the compounds formed in case of hydrated cement specimens on ageing. It was observed that the rate of the formation of the cementitious products in the former case appeared to be less. The significant fact to be noted here is that the type of calcium silicate hydrate formed during ageing was not same as indicated by presence of 2 Å peak in the hydrated soil - cement while this peak was absent in the case of hydrated cement. In the former the calcium silicate hydrate formed was CSHII while in the latter CSHI was the species for this product.

Appearance of hydrogarnet was also confirmed in the electron micrographs. Continued decrease of the characteristic peak of gehlenite hydrate (C_2ASH_8) with simultaneous growth of products such as ettringite and hydrogarnet indicated the metastable nature of gehlenite hydrate. In the present work it was observed that a conversion of gehlenite hydrate in the cement-stabilized soil specimens on ageing was mostly to the hydrogarnet with less of ettringite formed when the cement content was less. On the other hand, it was observed that ettringite was the major product with less of hydrogarnet when cement was more. Hence hydrogarnet plays a significant role in the strength development in the soil stabilized with lower percentage of cement. Conversion of C_2ASH_8 into hydrogarnet and ettringite was reported earlier (Locher, 1962).

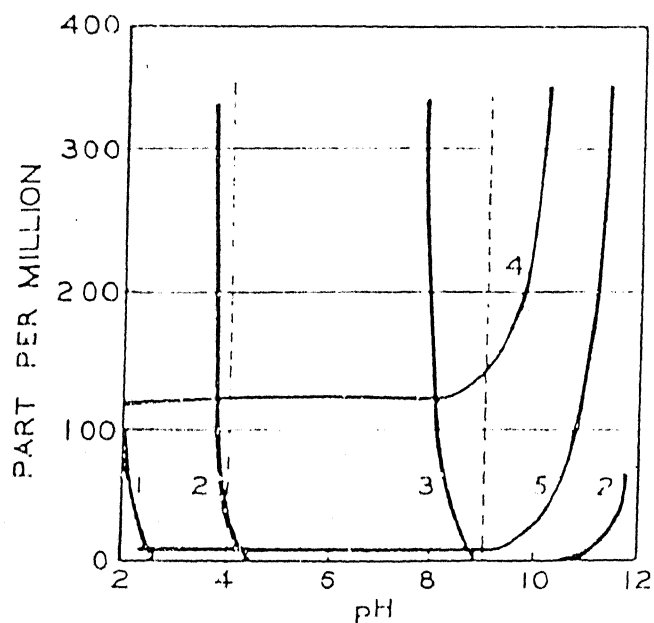
Participation of cement in the formation of cementitious products both in the case of hydrated FLG cement as well as soil stabilized with hydrated FLG cement was confirmed from the drastic reduction of lime peaks in the x-ray diffraction patterns of the respective specimens aged to different periods. Rate of consumption of lime was somewhat less upto an initial period of 7 days, but a drastic reduction in the intensities of the peaks for lime in specimens aged to 28 days indicated growth of reaction products in increased amounts between 7 and 28 days. High rate of consumption of lime can also be observed by faster rate of decrease of pH of the system (Tables 6.3 and 7.1).

Table 7.1

pH Values of Cement Specimens on Ageing

Specimen	Fresh	3 days	7 days	14 days	28 days
FLG cement having 20 % calcined gypsum	13.19	13.19	13.18	13.07	12.90

Several workers have earlier reported on the strength variation in stabilized soil-cement, but not many of them have tried to correlate the strength with pH variation. As seen in the solubility curve (Fig. 7.1), SiO_2 dissolves in alkaline solutions when the pH exceeds 10.5 to 11.0. This reaction involves depolymerization of silica through hydration and dissolution to Si(OH)_4 followed by addition of OH^- to form silicate ions. In the case of aluminium, the precipitation as the hydroxide is complete between pH 6.0 and 7.5. Aluminium hydroxide is an amphoteric electrolyte and redissolves in alkali at a pH of 10.9 to form soluble aluminates. The strength behaviour observed for soil stabilized with different percentages of FLG cement and aged upto 28 days clearly reflects the role of pH in the reaction and formation of the products. The high pH observed even at 28 days



1. FERRIC HYDROXIDE.
2. ALUMINIUM HYDROXIDE.
3. FERROUS HYDROXIDE.
4. AMORPHOUS SILICA.
5. QUARTZ

Fig. 7.1 Solubility of hydroxides and quartz at 25°C (after Pickering, 1962).

for soil samples stabilized with 12 %, 16 % and 20 % of cement explains the formation of increased amounts of different calcium and aluminium silicate hydrates as observed in the x-ray patterns.

Electron microscopy has enabled recognition of the mode of growth for the reaction products. The reaction appears to have been initiated around the grain boundaries and progressing with time towards the grain interior. In the early stages the products appears as coatings of the grains. With time, products like tobermorite and ettringite stand out from the grain surfaces exhibiting their respective morphological forms. With continued ageing upto 28 days, distinct fabric modification in the specimens of soil-cement system could be evidenced.

FLG cement has been proved in the present work to have immense scope in stabilizing a red soil. Strength gain in the soil-cement system (with cement varying from 12 to 20 %) is of the order of about 15 to 20 times the original strength of the soil. In addition, the stabilized soil has greater resistance to erosion (due to increased intergranular bonding) and relatively impervious to water.

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